(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
4 September 2003 (04.09.2003)

PCT

(10) International Publication Number
WO 03/072838 A1

(51) International Patent Classification[7]: C22C 19/03, C01B 6/00, H01M 4/38

(21) International Application Number: PCT/CA03/00058

(22) International Filing Date: 17 January 2003 (17.01.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2,373,553 27 February 2002 (27.02.2002) CA

(71) Applicant (*for all designated States except US*): **HERA, HYDROGEN STORAGE SYSTEMS INC.** [CA/CA]; 577 Le Breton, Longueuil, Quebec J4G 1R9 (CA).

(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **LIANG, Guoxian** [CA/CA]; 2776 Belcourt, Longueuil, Quebec J4M 1Y7 (CA). **SCHULZ, Robert** [CA/CA]; 68 Bel Horizon, Ste Julie, Quebec J3X 1S1 (CA).

(74) Agent: **ROBIC**; 55 St Jacques, Montreal, Quebec H2Y 3X2 (CA).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for the following designations AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZM, ZW, ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)*
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations*
— *of inventorship (Rule 4.17(iv)) for US only*

Published:
— *with international search report*
— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 03/072838 A1

(54) Title: Ca, Mg AND Ni CONTAINING ALLOYS, METHOD FOR PREPARING THE SAME AND USE THEREOF FOR GAS PHASE HYDROGEN STORAGE

(57) Abstract: Disclosed are new Ca, Mg and Ni-containing alloys of the general formula: $(Ca_c Mg_d M_e)_b (Ni_{1-z} T_z)_a$ where: M is at least one metal selected from the group consisting of Y, Ce, La, Pr, Nd, Th, Nd, Ti, V, Zr, Ta, Hf, Sr, Ba and Misch metals; T is at least one element selected from the group consisting of Al, Zn, Cu, Fe, Co, Mn, Cr, Mo, W, Si, Ga, Ge, In, Sn, Ag, C and B; a is an integer equal to 2 or 5; z is a number ranging from 0 to 0.5; when a is equal to 2, then $0.9 \leq b \leq 1.1$; and when a is equal to 5, then either $1.75 \leq b \leq 2.25$ or $0.75 \leq b \leq 1.31$. These alloys which are of the AB_2, A_2B_5 or AB_5 types, may be single phase or multiphase and are useful for reversibly absorbing hydrogen from a gas phase. Also disclosed is a method for preparing the above alloys.

Ca, Mg AND Ni CONTAINING ALLOYS, METHOD FOR PREPARING THE SAME AND USE THEREOF FOR GAS PHASE HYDROGEN STORAGE

Field of the invention

The present invention is directed to Ca, Mg and Ni-containing alloys. It is also directed to a method for preparing these alloys and to their use for reversibly absorbing hydrogen from a gas phase.

Background of the Invention

The use of hydrogen gas as a fuel for PEM fuel cells has received considerable attention in recent years because PEM fuel cells using pure hydrogen can provide high efficiency and ultra clean power. Unfortunately, widespread use of hydrogen energy is not currently feasible because of economic and technological barriers. One of the important barriers is the lack of cost effective, safe hydrogen storage method.

Hydrogen gas is very light. It can be compressed under high pressure and stored in pressurized vessels. It can also be liquefied and stored in liquid form. Hydrogen also reacts with metal or non-metals to form hydrides. Some metal hydrides called "low temperature metal hydrides" are reversible at ambient temperature and pressure. From a safety point of view, metal hydrides are intrinsically safe since the hydrogen must be released from the hydrides before it can burn or be oxidized. The volumetric density of hydrogen storage in metal hydrides is usually high.

The most serious shortcomings of the reversible metal hydrides and more particularly the low temperature metal hydrides are their low gravimetric

storage density and the high cost. For stationary and some mobile applications, the weight of the hydrogen storage tank is not a problem. However, the high cost of conventional low temperature metal hydrides results in too expensive storage devices.

Amongst the known hydrogen storage materials, conventional lanthanum or mischmetal-based alloys of the AB_5 type like $LaNi_5$ alloys are inherently expensive because they make use of a rare earth metal. $CaNi_5$ is isomorphic to $LaNi_5$ and has higher storage capacity than that of $LaNi_5$ based hydrides. In the Ca-Ni system, there are four stable compounds, $CaNi_2$, $CaNi_3$, Ca_2Ni_7 and $CaNi_5$, but only the $CaNi_5$ has been considered to be of practical interest since the plateau pressures of $CaNi_5$ are adequate for applications. The other three compounds do form very stable hydrides. However, hydrogen can not be extracted at temperatures below 100°C under normal pressure.

In a paper published in 1980 (and identified A in the attached list of references), Osterreicher et al disclosed a $Ca_{0.5}Mg_{0.5}Ni_2$ alloy prepared by liquid sintering in a Ta tube. They also disclosed that such a $Ca_{0.5}Mg_{0.5}Ni_2$ alloy can absorb hydrogen to form $Ca_{0.5}Mg_{0.5}Ni_2H_{2.6}$ at 300°K (corresponding to 1.7 wt.%). However, this hydride can only desorbs partially (half of the amount absorbed) at 400°K and 1bar. The desorption isotherm is strongly sloped. According to these authors, the low reversibility of this alloy limits practical applications. However, this publication teaches that substitution of Ca by Mg in $CaNi_2$ is possible. The alloys of the type $Ca_xMg_{1-x}Ni_2$ are predominantly of $CaNi_2$ structure (C15 type) when x is larger or equal to 0.5.

In a recent paper (B) Terashita et al. disclosed a $Ca_xMg_{1-x}Ni_2$ system. Moreover, they presented results of tests made on a $Ca_{0.33}Mg_{0.67}Ni_2$ alloy prepared by high frequency induction melting. Once again, the plateau pressure of this alloy $Ca_{0.33}Mg_{0.67}Ni_2$ is still too low for most gas phase

applications and it is impossible to raise the plateau pressure by substituting more Mg for Ca using the induction melt casting method because the $MgNi_2$ phase precipitates. That phase is known for not absorbing hydrogen and consequently the properties deteriorate.

Since Ca and Mg have very high evaporation rate, it is very hard to produce a stoichiometric Ca-Mg-Ni alloy in large quantity. For example, if use is made of a melt casting method, the Mg and Ca alloy in liquid form has to be protected by argon or SF_6 because of the rapid oxidization and possible explosion. The composition has to be adjusted by trial and error due to evaporation loss of Mg and Ca. The so-cast alloys usually have very high macro-segregation and micro-segregation. Homogenization by long annealing treatments is required but adds costs to the alloys. In paper A, the Ca-Mg-Ni alloys were synthesized by liquid phase sintering in closed Ta tubes starting from elemental Mg, Ca and Ni at a temperature below 1250°C. Such a method also needs high temperature and long sintering time to reach complete reaction.

Mg-Ca-Ni alloys of the AB_3 type have also been synthesized by a powder sintering method. In a recent publication (C), Kadir et al disclosed a $CaMg_2Ni_9$ ternary alloy prepared by sintering fine powder mixtures of $MgNi_2$ and $CaNi_5$. This paper states that the sintering process involved raising the temperature stepwise to 600°C, 850°C and 990°C (in 0.6MPa Ar gas), with set temperature holds for 2-3h. Several attempts were necessary until an optimum composition was found. A slight excess of $CaNi_5$ over the stoichiometric composition was necessary in order to compensate for the evaporative loss of Ca.

Mg and Ca are known to react with all type of ceramic crucible at elevated temperatures and Ni is known to react with refractive metals at high temperatures. Therefore, all the sintering of alloys containing Mg, Ca and

Ni were performed so far in Mo or Ta crucible, especially when long sintering times were needed. In practice, this means that the use of this technology would be expensive.

Summary of the invention

The present invention as claimed hereinafter relates to new Ca, Mg and Ni-containing alloys of the general formula:

$$(Ca_c Mg_d M_e)_b (Ni_{1-z} T_z)_a$$

where:

M is at least one metal selected from the group consisting of Y, Ce, La, Pr, Nd, Th, Nd, Ti, V, Zr, Ta, Hf, Sr, Ba and Misch metals;

T is at least one element selected from the group consisting of Al, Zn, Cu, Fe, Co, Mn, Cr, Mo, W, Si, Ga, Ge, In, Sn, Ag, C and B;

a is an integer equal to 2 or 5

z is a number ranging from 0 to 0.5, and

when a is equal to 2, then b, c, d, e are numbers selected so that:

$0.9 \leq b \leq 1.1$

$c = 0.4-x$,

$d = 0.6-y$, and

$e = x + y$, with

$-0.4 < y \leq 0.5$

$-0.5 \leq x < 0.4$, and

$x + y > 0$;

when a is equal to 5, then b, c, d, e, are numbers selected so that

<u>either</u>

$1.75 \leq b \leq 2.25$

$c = 0.4-x$,

$d = 0.6-y$, and

$e = x+y$, with
$-0.4 \leq x \leq 0.2$,
$-0.2 \leq y \leq 0.4$, and
$x+y \geq 0$
<u>or</u> $0.75 \leq b \leq 1.31$,
$c = 0.6-y$,
$d = x+y$, and
$e = 0.4-x$, with
$-0.6 < x < 0,4$,
$-0.4 < y < 0.6$, and
$0 < x+y \leq 0.5$

When a is equal to 2, the alloys according to the invention can be said to be of the AB_2 type.

When a is equal to 5 and b is ranging between 1.75 and 2.25, the alloys according to the invention can be said to be of the A_2B_5 type.

When a is equal to 5 and b is ranging between 0.75 and 1.31, the alloys according to the invention can be said to be of the AB_5 type.

In all cases, the alloys may be single phase or multiphase.

The invention also relates to a method for preparing the above mentioned alloys, comprising the steps of:
- milling a mixture of elemental powders and/or pre-alloyed combination of elemental powders of Ca, Mg, M, Ni and T in relative amounts corresponding to those found in the requested alloy; and
- annealing and/or sintering the so-milled mixture of powders at a temperature higher than 800°C to obtain the requested alloy.

The invention further relates to the use of the above-mentioned alloys for reversibly absorbing hydrogen from a gas phase.

The invention and its advantages will be better understood upon reading the following non-restrictive description and examples made with reference to the accompanying drawings.

Brief description of the drawings

With respect to the alloys of the AB_2 type:

Fig. I-1 shows the XRD (x-ray diffraction) spectra of a sample of composition $Ca_{0.4}Mg_{0.6}Ni_2$ made by milling a powder mixture of Ca, Mg and Ni powders as a function of milling time.

Fig.I-2 shows the XRD spectra of a series of $Ca_xMg_{1-x}Ni_2$ samples for x=0, 0.2, 0.4, 0.5, 0.7and 1 obtained after 20h of milling.

Fig.I-3 shows the XRD spectra of a mechanically alloyed $Ca_{0.3}Mg_{0.7}Ni_2$ sample annealed for 1 hour at different temperature 600°C, 800°C and 1000°C.

Fig.I-4 shows the XRD spectra of mechanically alloyed $Ca_xMg_{1-x}Ni_2$ for x=0, 0.2, 0.3, 0.4 and 0,8 after 1h annealing at 1000°C.

Fig.I-5 shows PCT (pressure-concentration isotherm) of $Ca_xMg_{1-x}Ni_2$ alloys measured at 30°C.

Fig.I-6 shows the XRD spectra of Zn (on the B site) and Mm (on the A site) substituted $Ca_{0.4}Mg_{0.6}Ni_2$ alloy after annealing at 1000°C for 1h.

Fig.I-7 shows the XRD spectra of Cu and Fe (on the B site) and Mm (on the A site) substituted $Ca_{0.3}Mg_{0.7}Ni_2$ alloy after annealing at 1000°C for 1h.

Fig.I-8 shows the PCT of various $(Ca_{0.4-x}Mg_{0.6-y}Mm_{x+y})Ni_2$ substituted alloys.

Fig.I-9 shows the position of the plateau pressures versus the lattice parameters for various $Ca_xMg_{1-x}Ni_2$ alloys and $(Ca_xMg_{0.7}Mm_y)Ni_2$. The

substitution of Ca by Mm does not change much the lattice parameter but increases significantly the plateau pressures.

With respect to the alloys of the A_2B_5 type:

Fig.II-1 shows the XRD spectra of $(Ca_{0.4}Mg_{0.6})_2Ni_5$ after ball milling for various time using process A (i.e. starting with a mixture of intermetallics and elemental powders).

Fig.II-2 shows the XRD spectra of $(Ca_{0.4}Mg_{0.6})_bNi_5$ for various A/B=b/5 ratios after annealing at 1000°C.

Fig.II-3 shows the XRD spectra of $(Ca_{0.375}Mg_{0.625})_2Ni_5$ made by process B (i.e. by milling elemental powder of Ca, Mg and Ni) and annealed 1h at various temperature.

Fig.II-4 shows the PCT curves measured at 30°C of $(Ca_{0.375}Mg_{0.625})_2Ni_5$ annealed at various temperatures.

Fig.II-5 shows the PCT curves of $(Ca_{0.375}Mg_{0.625})_2Ni_5$ annealed at 1000°C and measured at various temperatures.

Fig.II-6 shows the XRD spectra of various $(Ca_xMg_y)_2Ni_5$ with various Mg/Ca ratios.

Fig.II-7 shows the PCT curves measured at 30°C of the various samples shown in Fig.II-5.

Fig. II-8 shows the XRD spectra of various Mm substituted $(Ca_{0.375-x}Mg_{0.625-y}Mm_{x+y})_2Ni_5$ – Substitution on the A site.

Fig.II-9 shows the PCT curves of the various substituted alloys shown in Fig.II-8.

Fig.II-10 shows the XRD spectra of $(Ca_{0.5}Mg_{0.375}Mm_{0.125})_2Ni_5$ and its hydride.

Fig.II-11 shows the XRD spectra of various A_2B_5 type alloys with substitution on the B site.

Fig.II-12 shows the PCT curves of various substituted alloys shown in Fig.II-11.

<u>With respect to the alloys of the AB_5 type:</u>

Fig.III-1 shows the XRD spectra of $Ca_xMm_{1-x}Ni_5$ alloys made by mechanical alloying followed by annealing

Fig.III-2 shows the lattice parameters of the $Ca_xMm_{1-x}Ni_5$ alloys shown in Fig.III-1.

Fig. III-3 shows representative PCT curves of some of the ternary $Ca_xMm_{1-x}Ni_5$ alloys shown in Fig.III-1.

Fig.III-4 a&b show XRD spectra of ball milled Ca-Mg-Ni ternary alloys before and after annealing treatment and demonstrate that the solubility of Mg in $CaNi_5$ is very low.

Fig.III-5 a&b show XRD spectra of ball milled Mm-Mg-Ni ternary alloys before and after annealing treatment and demonstrate that the solubility of Mg in $MmNi_5$ is also very low.

Fig.III-6 shows XRD spectra of various mechanically alloyed Mm-Ca-Mg-Ni quaternary alloys before annealing treatment.

Fig.III-7 shows XRD spectra of various mechanically alloyed Mm-Ca-Mg-Ni quaternary alloys after annealing treatment.

Fig.III-8 shows the PCT curves of the quaternary alloys shown in Fig.III-7

Fig.III-9 a&b shows the XRD spectra of various Mm-rich quaternary Mm-Ca-Mg-Ni alloys (a) and the corresponding PCT curves (b).

Fig.III-10 a&b show the XRD spectra of various Mm-poor quaternary Mm-Ca-Mg-Ni alloys (a) and the corresponding PCT curves (b).

Fig.III-11 shows the relationship between the plateau pressure and the c/a parameter of various $(Mm\text{-}Ca\text{-}Mg)_bNi_5$ alloys.

Detailed description of the invention

1. ALLOYS OF THE AB_2 TYPE

As aforesaid, when a is equal to 2, then the alloys according to the invention are of the formula:

$$(Ca_{0.4-x}Mg_{0.6-y}M_{x+y})_b(Ni_{1-z}T_z)_2$$

where M and T are defined as above and
$0.9 \leq b \leq 1.1$,
$-0.5 \leq x \leq 0.4$,
$-0.4 < y \leq 0.5$,
$x + y > 0$; and
$0 \leq z \leq 0.5$.

Preferably:

$-0.1 \leq x \leq 0.25$; and
$-0.1 \leq y \leq 0.15$.

These alloys are single or multiphase hydrogen storage compounds of the AB_2 type, which are capable of absorbing and desorbing hydrogen from a gas phase at ambient temperature with a flat plateau pressure and a storage capacity larger than 1.2 wt %.

These alloys may be prepared by a method comprising the following two steps.
The first one consists of preparing a powder by milling a mixture of elemental powders and/or pre-alloyed combination of the elemental powders (ex.: Ca, Mg, Ni, Mm, $CaNi_2$, $MgNi_2$, $MmNi_5$, when M = Mm) in respective

amounts selected to obtain the requested alloy. The milling can be a conventional ball milling or a more intensive mechanical alloying that can be carried out at room temperature or at high temperatures with or without anti-sticking agents and in various kind of atmosphere.

The second step consists of annealing and/or sintering the milled powder at elevated temperatures in a crucible made of, for example, stainless steel, for a short period of time in an inert or reactive atmosphere. This is an essential step to achieve a high reversible absorption capacity and a flat plateau. The annealing temperature should be higher than 800°C but not higher than 1050°C.

The invention is based on the discovery that the mechanical alloying of elemental powders (such as powders of Ca, Mg, Ni) and/or of mixtures of intermetallic compounds (such as powders of $CaNi_5$, $MgNi_2$) corresponding to the composition of the formula:

$$Ca_xMg_{1-x}Ni_2$$

leads to a nanocrystalline ternary intermetallic compound with the $CaNi_2$ structure (C15-type) for $x \geq 0.3$. This so-milled nanocrystalline alloy can reversibly absorb and desorb hydrogen at room temperature. However, the reversible absorption capacity is small and the slope of the PCT curves is very big like in the case of conventional large-grain polycrystalline $Ca_xMg_{1-x}Ni_2$ alloys already reported in the art (see reference B).

The invention is also based on the discovery that, when a thermal treatment) of the present invention is applied to this mechanically alloyed powder, a substantial improvement in properties is achieved. Indeed, the hydrogen storage properties of the mechanically alloyed Mg-Ca-Ni are substantially improved by annealing the powder at temperatures higher than 800°C for short period of time, typically at 1000°C or slightly higher, for

0.5h to 1h. Annealing at temperatures lower than 800°C does not improve the hydrogen storage properties very much.

The ball milling time can vary from a few minutes to several hours. When the milling time is of about 10 hours, then a true alloy is formed between the components (see Fig.I-1), i.e. a nanocrystalline ternary intermetallic compound with the $CaNi_2$ structure (C15-type)). Thus, in that case, the ball milling step is a mechanical alloying. Under these conditions, the post-thermal step becomes an annealing treatment which could be as short as 0.5 to 1 hour as indicated above.

On the other hand, when the ball milling step is only carried out for a few minutes, the powder particles are then only agglomerates of the various constituents. In that case, the post-thermal step is a sintering treatment which could take a few hours to produce the final alloy product.

Further improvements to these alloys may be achieved by adding other elements to Ca, Mg and Ni or their combinations. Such an addition may raise the plateau pressure and improve hydrogen storage properties such as plateau slope and the long-term stability while keeping the AB_2 (C15-type) structure as the main phase.

<u>Example I-1</u>: Compound according to the prior art made by the method according to the invention

$Ca_{0.3}Mg_{0.7}Ni_2$ (b = 1, x= 0.1, y= -0.1, z= 0) was synthesized in a SPEX® high energy ball mill under the protection of argon. A Mg powder (>99%, + 100mesh), Ca granules (>99.5, ~2mm in size) and a Ni powder (<99.9%, -325mesh) were used as starting materials.

Isothermal annealing was performed in a tubular furnace under the protection of argon flow. The mechanically alloyed powder was sealed in a stainless steel crucible before annealing. The powder was heated to 1000°C at a heating rate of 30C/min, and held at 1000°C for 1 hour, then cooled down to room temperature in the furnace.

Hydrogen absorption/desorption properties were measured by using an automatic Sievert's type apparatus. The annealed powder normally needs mild activation treatment, such as heated to 200°C under vacuum and then cooled down. EDX analysis shows that the Fe content in the end product less than 0.2 at.%. The composition of the end product was close to the nominal composition. The activated alloy exhibited a relatively flat plateau and a high capacity.

Example I-2: Compound according to the invention made by the method according to the invention

$Ca_{0.15}Mg_{0.7}Mm_{0.15}Ni_2$ (x= 0.25, y= -0.1, M= Mm, x+y= 0.15, b= 1, z= 0) was synthesized by mechanical alloying of elemental powder blends. The alloy was annealed in the same manner as in Example 1. This alloy had a hydrogen storage capacity of 1.25wt.%. The plateau pressure was drastically raised, and the plateau slope was much less than that of $Ca_{0.3}Mg_{0.7}Ni_2$ of the example I-1

Examples I-3 and subsequent

Other examples similar to example 1-2 were carried out. The results of these other examples are reported in the accompanying drawings (see Figs. I-1 to 9).

2. ALLOYS OF THE A_2B_5 TYPE

As aforesaid, when a is equal to 5, then the alloys according to the invention may be of the formula:

$$(Ca_{0.4-x}Mg_{0.6-y}M_{x+y})_b(Ni_{1-z}T_z)_5$$

where M and T are defined as above and

$1.75 \leq b \leq 2.25$,
$-0.4 \leq x \leq 0.2$,
$-0.2 \leq y \leq 0.4$,
$x+y \geq 0$, and
$0 \leq z \leq 0.5$.

Preferably:

$-0.1 \leq x \leq 0.1$, and
$-0.1 \leq y \leq 0.2$.

Preferably also, Mg and Ca are present in a Mg/Ca ratio ranging from 0.5 to 2 and more preferably from 1.5 to 1.75.

As mentioned before, in a Ca-Ni system, there are four stable compounds $CaNi_2$, $CaNi_3$, Ca_2Ni_7 and $CaNi_5$.The $CaNi_2$ –type system (also called AB_2) has been the subject of PART I hereinabove. This system has a cubic C15 structure and Mg can substitute Ca up to $x=0.3$ in the $Ca_xMg_{1-x}Ni_2$ alloys while maintaining a cubic structure. The unit cell volume decreases and the plateau pressure increases with increasing the Mg content.

In accordance with the invention, it has been found that the replacement of Ca and/or Mg by Mm in a quaternary AB_2 type Ca-Mg-Mm-Ni system improves the hydrogen storage properties significantly

$CaNi_3$ type alloys have been investigated in great details. The intermetallic compound $CaNi_3$ can absorb hydrogen readily to form $CaNi_3H_{4.6}$ but cannot

release hydrogen under ambient conditions (see reference A). Oesterreicher et al. have investigated the pseudo-binary $Ca_xMg_{1-x}Ni_3$ and found that Mg can substitute Ca up to x= 0.7(see again reference A). Recently, Kadir et al. reported a series of AB_3 alloys of the type AB_2C_9 identified as RMg_2Ni_9 where (R= La, Ce, Pr, Nd, Sm and Gd) (reference D) and a $CaMg_2Ni_9$ alloy (reference C) synthesized by sintering a mixture of elemental powders or intermetallic compounds. They found that these AB_2C_9 type compounds have the $PuNi_3$ structure (reference D). The unit cell volume and hydrogen storage properties can be altered by different substitutions for the A, B and C elements.

In between $CaNi_2$ and $CaNi_3$, a metastable Ca_2Ni_5 compound with an hexagonal P63/m structure (space group 176) has previously been reported (see reference E). This material was prepared from the melt by a peritectic reaction at 1035°C. The present inventors have not been able to synthesize this compound by using the method of preparation described in this document but have discovered that when one substitutes some Ca by Mg in the virtual Ca_2Ni_5 compound, a new phase having a structure different from those of AB_2 ($MgCu_2$ – cubic), AB_3 ($PuNi_3$ – hexagonal) and Ca_2Ni_5 (BaC6 – hexagonal) is formed when the compound is prepared by the method of the present invention. This new phase has a large hydrogen storage capacity and an adequate plateau pressure for reversibly storing hydrogen gas at room temperature.

Therefore, the second range of composition encompassed by the present invention is the range where the A/B ratio is between 0.45 and 0.35. As mentioned previously, A means $(Ca_{0.4-x}Mg_{0.6-y}M_{x+y})$ and B means $(Ni_{1-z}T_z)$. This range corresponds to alloys of the A_2B_5 type.

As discussed hereinabove, a AB_2 phase with a cubic C15 structure is formed when the A/B ratio is bigger than 0.45. When the A/B ratio is less

than 0.35, an AB_3 phase with the $PuNi_3$ structure is formed. However, when the A/B ratio is in the range of 0.35-0.45, a new A_2B_5-type phase with a crystallographic structure which has not yet been identified, is obtained. This new alloy is made by the same method as the one discussed previously, which comprises first preparing a powder by milling a mixture of elemental powders and/or pre-alloyed combinations of elemental powders (ex.: Ca, Mg, Ni, $CaNi_2$, $MgNi_2$ ...) in amounts sufficient to achieve the requested composition, and then annealing and/or sintering the so milled mixture at an elevated temperature of about 1000°C to form the requested hydrogen storage alloy.

Thus, the invention is based on the discovery of new hydrogen storage alloys of the A_2B_5 type which contains Ca, Mg, Ni and other optional elements. These new alloys are capable of absorbing and desorbing hydrogen from the gas phase at ambient temperature with a flat plateau pressure and a storage capacity larger than 1.5 wt%.

These alloys may be prepared by a method comprising two steps.

The first one consists of preparing a powder by milling a mixture of elemental powders and/or pre-alloyed combinations of the elemental powders (ex.: Ca, Mg, Ni, Mm, $CaNi_2$, $MgNi_2$, $MmNi_5$, when M=Mm) in respective amounts selected to obtain the requested alloy. The milling can be a conventional ball milling or a more intensive mechanical alloying. It can be carried out at room temperature or at high temperatures with or without anti-sticking agents and in various kinds of atmosphere.

The second step consists of annealing and/or sintering the milled powder at elevated temperatures in a crucible made of, for example, stainless steel, for a short period of time in an inert or reactive atmosphere. This is an essential step to achieve high reversible capacity and a flat plateau. The annealing

temperature should be higher than 900°C but not higher than 1080°C.

Once again, the invention is based on the discovery that mechanical alloying of elemental powders (such as Ca, Mg, Ni) and/or mixtures of intermetallic compounds (such as $CaNi_5$, $MgNi_2$) corresponding to the requested composition $(Ca_xMg_{1-x})_2Ni_5$ leads to a highly disordered structure when the Mg/Ca ratio is between 0.33 and 1.67. The so-milled alloy can reversibly absorb and desorb hydrogen at room temperature. However, the reversible capacity is small and the slope of the PCT curves is very big.

The invention is also based on the discovery that a new A_2B_5 type phase is formed when the mechanically alloyed $(Ca_xMg_{1-x})_2Ni_5$ is annealed at temperature above 600°C. The formation range of this new phase depends on the Mg/Ca ratio and the (Ca+Mg)/Ni ratio. For a stoichiometric A_2B_5 composition, the new phase no longer forms when the Mg/Ca ratio is lower than 0.3. If the Mg/Ca ratio is higher than 1.75, a large amount of $MgNi_2$ phase is formed and, as a result, the storage capacity is reduced. When the Mg/Ca ratio is set at 1.5, the new phase is formed when the (Mg+Ca)/Ni ratio is between 0.35 and 0.45.

The invention is further based on the discovery that when a thermal treatment is applied to this mechanically alloyed powder, substantial improvement in properties is achieved. Indeed, the hydrogen storage properties of the ball milled Ca-Mg-Ni are significantly improved by annealing the powder at temperatures higher than 900°C preferably around 1000°C or slightly higher for a short period of time, preferably 0.5 to 1 hour. Annealing at temperatures lower than 900°C does not improve the hydrogen storage properties very much.

It has also been discovered that further improvements are achieved by adding other elements to the basic elements used for preparing the alloys. Such an addition raises the plateau pressure and improves other hydrogen storage properties such as plateau slope and the long term stability .

Example II-1

$(Ca_{0.375}Mg_{0.625})_2Ni_5$ (x=0.025, y= -0.025, b=2, z=0) was synthesized in a SPEX high energy ball mill under an argon protective atmosphere. A Mg powder (> 99%, +100mesh), Ca granules (>99.5%, 2mm in size) and a Ni powder (>99.9%, -325mesh) were used as starting materials. Isothermal annealing was performed in a tubular furnace under argon. The mechanically alloyed powder was sealed in a stainless steel crucible before annealing. The powder was heated to 1000°C at a heating rate of 30°C/min, held at 1000°C for 1 hour and then cooled down to room temperature in the furnace.

Hydrogen absorption/desorption properties were measured by using an automatic Sievert's type apparatus. The annealed powder normally needs a mild activation treatment, such as a heating treatment to 200°C under vacuum followed by a cooling. EDX analysis showed that the Fe content in the end product is less than 0.2 at.%. The composition of the end product was close to the nominal composition. The activated alloy exhibited a relatively flat plateau and a high capacity

Example II-2

$(Ca_{0.3125}Mg_{0.625}Mm_{0.0625})_2Ni_5$ (x= 0.0875, y= -0.025, M=Mm, x+y= 0.0625, b=2, z=0) was synthesized by ball milling of elemental powder blends. The alloy was annealed in the same manner as in Example II-1. This alloy had a storage capacity of 1.65wt%. Its plateau pressure was flat and

significantly raised as compared to that of Example II-1.

Example II-3 and subsequent

Other examples similar to examples II-1 and 2 were carried out. The results of these other examples are reported in the accompanying drawings (see Figs. II-1 to 12).

3. ALLOYS OF THE AB_5 TYPE

As aforesaid, when a is equal to 5, then the alloys according to the invention may also be of the formula:

$$(Ca_{0.6-y}Mg_{x+y}M_{0.4-x})_b(Ni_{1-z}T_z)_5$$

when M and T are defined as above and
$0.75 \leq b \leq 1.31$,
$-0.6 < x < 0.4$,
$-0.4 < y < 0.6$,
$0 < x+y \leq 0.5$, and
$0 \leq z \leq 0.5$.

Preferably:
$-0.2 \leq x \leq 0.2$,
$-0.2 \leq y \leq 0.2$, and
$0.1 \leq x+y \leq 0.4$

Alloys of the AB_3 type have already been studied in great detail (see references C, D, F, G, H). Some of them have even been recently patented for battery applications (see references I and J). For example, the patent identified as reference I discloses alloys of the formula $(Mg_{1-a-b}R1_aM1_b)Ni_z$

where $3 \leq z \leq 3.8$. Such corresponds to alloys AB where the ratio A/B is ranging between 0.263 and 0.33.

The alloys according to the invention as defined hereinabove are of the AB_5 type. $LaNi_5$- and $MmNi_5$- based AB_5 type alloys have been widely investigated as hydrogen storage materials (see reference 1 and 2). The La, Mm and Ni atoms can be substituted by many other elements to tailor the hydrogen storage properties for different applications (see reference 3). However, substitution of La by Mg in $LaNi_5$ has not been successful. A second phase with an approximate composition of $LaMg_{1.85}Ni_{9.26}$ was found with a nickel-rich $LaNi_{5+x}$ main phase in a melt casting $Mg_{0.1}La_{0.9}Ni_5$ sample (see reference 4). The hydrogen storage capacity was reduced due to the formation of this second phase.

$CaNi_5$ intermetallic compound represents a category of low cost hydrogen storage materials with a storage capacity up to 1.9wt.% (see references 5 to 7). However, little attention has been paid so far to such a system, probably due to its well-known bad cycling stability (see reference 8). Improvement of the hydrogen storage properties of $CaNi_5$ by substitution of Ca or Ni with other elements has been tried (see references 5 to 8; A and K). Ternary $Ca_xMm_{1-x}Ni_5$ alloys were produced by melt casting and were also investigated (see reference 5). Mm substitution for Ca can raise the plateau pressure of $CaNi_5$. However, the plateau slope is big for the as-cast ternary alloys due to segregation. Annealing at elevated temperatures (>1000°C) can reduce the slope to some extent. Previous works made by the present inventors have shown that $CaNi_5$ and Mm or Zn-substituted $CaNi_5$ type alloys with relatively flat plateau can be produced by mechanical alloying followed by an annealing treatment at low temperatures (640C) (see reference L).

Substitution of Mg for Ca in a $CaNi_5$ structure has also been investigated. The reported results show that the $Ca_{1-x}Mg_xNi_5$ does not extend homogeneously beyond x=0.06 (see reference A).

The invention is based on the discovery that slight substitution of Mg in the $CaNi_5$ destroys the AB_5 structure, and a mixture of AB_3 and free nickel is formed. The hydrogen storage capacity is also reduced. However, when the alloy of the AB_5 type containing Mg comprises more than 3 elements, the solubility limit can be extended and the plateau can be tailored by the Mg content. The plateau slope is also small and the reversible hydrogen storage capacity is bigger in comparison to ternary Ca-Mm-Ni AB_5 type alloys.

Thus, the present invention provides new hydrogen storage alloys of the AB_5 type, which contains Ca, Mg, Ni and M. These alloys are capable of absorbing and desorbing hydrogen from a gas phase at ambient temperature with a flat plateau pressure and a storage capacity larger than 1.3wt.%.

These new alloys may be prepared by a method similar to those already disclosed, which comprises two steps.

The first step consists of preparing a powder by milling a mixture of elemental powders and/or pre-alloyed combination of the elemental powders (ex.: Ca, Mg, Ni, Mm, $CaNi_2$, $MgNi_2$, $MmNi_5$, when M=Mm) in respective amounts selected to obtain the requested composition. The milling can be a conventional ball milling or a more intensive or mechanical alloying which can be carried out at room temperature or at high temperatures with or without anti-sticking agents and in various kinds of atmosphere.

The second step consists of annealing and/or sintering the mechanically alloyed powder at elevated temperatures in a crucible made of, for example, stainless steel for a short period of time in an inert or reactive atmosphere.

This is an essential step to achieve high reversible capacity and a flat plateau. The annealing temperature should be higher than 800°C but not higher than 1100°C.

Once again, the invention is based on the discovery that mechanical alloying of elemental powders (such as Ca, Mm, Ni) and/or mixtures of intermetallic compounds (such as $CaNi_5$, $MmNi_5$) corresponding to the requested composition $Ca_xMm_{1-x}Ni_5$ leads to a nanocrystalline AB_5 type structure. The so-milled alloy can reversibly absorb and desorb hydrogen at room temperature. However, the reversible capacity is small and the slope of the PCT curves is very big.

The invention is also based on the discovery that when a thermal treatment is applied to this mechanically alloyed powder, substantial improvement in properties is achieved. Indeed, the hydrogen storage properties of the mechanically alloyed Mg-Ca-Ni are substantially improved when the powder is annealed at temperatures higher than 800°C typically at 1000°C or slightly higher, for short period of time, preferably 0.5h-1h. Annealing at temperatures lower than 800°C does not improve the hydrogen storage properties very much.

It has also been discovered that further improvements are achieved by adding other elements (M) to the basic elements used for preparing the alloys. Such an addition raises the plateau pressure and improves other hydrogen storage properties such as plateau slope and the long-term stability while keeping predominantly the AB_5-type structure.

<u>Example III- 1:</u> Compound according to the prior art made by the method according to the invention.

$Mm_{0.4}Ca_{0.6}Ni_5$ (x=0, y=0, b=1, z=0) was synthesized in a SPEX high

energy ball mill under an argon protective atmosphere. A Mm powder (>99%, + 100mesh), Ca granules (>99.5, ~2mm in size) and a Ni powder (<99.9%, -325mesh) were used as starting materials.

Isothermal annealing was performed in a tubular furnace under argon. The mechanically alloyed powder was sealed in a stainless steel crucible before annealing. The powder was heated to 1000°C at a heating rate of 30°C/min, held at 1000°C for 1 hour and then cooled down to room temperature in the furnace.

Hydrogen absorption/desorption properties were measured by using an automatic Sievert's type apparatus. The annealed powder normally needs mild activation treatment, such as a heating treatment to 200°C under vacuum followed by a cooling. EDX analysis shows that the Fe content in the end product is less than 0.3 at.%. The composition of the end product was close to the nominal composition. The activated $Mm_{0.4}Ca_{0.6}Ni_5$ alloy exhibited a relatively flat plateau and a high capacity.

Example III-2: Compound according to the invention made by the method according to the invention

$(Mm_{0.333}Ca_{0.5}Mg_{0.167})_{1.2}Ni_5$ (M = Mm, x = 0.067, y = 0.1, x + y = 0.167, b = 1.2 and b/5 = 0.24, z = 0) was synthesized by mechanical alloying of elemental powder blends. The alloy was annealed in the same manner as in Example III-1. This alloy had a hydrogen storage capacity of 1.45wt.%. The plateau pressure and reversible hydrogen storage capacity were significantly improved in comparison to those of the prior art alloy $Ca_{0.6}Mm_{0.4}Ni_5$.

Example III-3: Compound according to the invention made by the method according to the invention:

$(Mm_{0.333}Ca_{0.417}Mg_{0.25})_{1.2}Ni_5$ (M = Mm, x = 0.067, y = 0.183, x + y = 0.25, b = 1.2 and b/5 = 0.24, z = 0) was synthesized by mechanical alloying of elemental powder blends. The alloy was annealed in the same manner as in Example III-1. This alloy had a hydrogen storage capacity of 1.4wt.%. The plateau pressure was flat and even higher than the one of Example III-2.

Example III-4 and subsequent

Other examples similar to those of Examples III-2 and 3 were carried out. The results of these other examples are reported in the accompanying drawings (see Figs. III-1 to 11).

REFERENCES

(A) "Hydriding Behavior of Ca-Mg-Ni-B" by H. Oesterreicher, K. Ensslen, A. Kerlin and E. Bucher, Mat. Res. Bull., 15 (1980) 275

(B) "Structural and Hydriding Properties of $(Ca_xMg_{1-x})Ni_2$ Laves phases alloys" by N. Terashita, K. Kobayashi, T. Sasai, E. Akiba, J. of Alloys and Compounds 327 (2001) 275

(C) "Structural investigation and hydrogen capacity of $CaMg_2Ni_9$: a new phase in the AB2C9 system isostructural with LaMg2Ni9" by K. Kadir, N. Kuriyama, T. Sakai, I. Uehara, L. Ericksson, J. of Alloys and Compounds 284 (1999) 145

(D) "Synthesis and structure determination of a series of hydrogen storage alloys; RMg_2Ni_9 (R=La, Ce, Pr, Nd, Sm, and Gd) built from $MgNi_2$ Laves-type layers alternating with AB_5 layers", by K. Kadir, T. Sakai, I. Uehara, J. of Alloys and Compounds 257 (1997) 115

(E) International Centre for Diffraction Data, JCPDS File # 19-0243 on Ca_2Ni_5

(F) "Structural investigation and hydrogen storage capacity of $LaMg_2Ni_9$ and $(La_{0.65}Ca_{0.35})(Mg_{1.32}Ca_{0..68})Ni_9$ of the AB_2C_9 type structure" by K. Kadir, T. Sakai and I. Uehara, J. of Alloys and Compounds 302 (2000) 112

(G) "Hydriding properties of $LaNi_3$ and $CaNi_3$ and their substitutes with $PuNi_3$-type structure" by J. Chen, H.T. Takeshita, H. Tanaka, N. Kuriyama, T. Sakai, I. Uehara, M. Haruta, J. of Alloys and Compounds 302 (2000) 304

(H) "Hydrogen storage properties of new ternary system alloys: La_2MgNi_9, $La_5Mg_2Ni_{23}$, La_3MgNi_{14}" by T. Kohno, H. Yoshida, F. Kawashima, T. Sakai, M. Yamamoto and M. Kanda, J. of Alloys and Compounds 311 (2000) L5

(I) "Hydrogen-Absorbing Alloy" US Patent No. 6,130,006 (2000)

(J) Japanese Patent JP 11-217643 (1999)

(K) J.O. Jensen, N.J. Bjerrum, J. of Alloys and Compounds, 293 (1999) 185

(L) G. Liang, J. Huot and R. Schulz, J. of Alloys and Compounds 321 (2001) 146

(1) K.H. Buschow, in Handbook on the Physics and Chemistry of Rare Earths, vol.6, edited by K.A. Gschneider, Jr. and L. Eyring, Elsevier Science Publishers, B.V. (1984) chap 47

(2) T. Sakai, in Handbook on the Physics and Chemistry of Rare Earths, vol. 21, edited by K.A. Gschneider, Jr. and L. Eyring, Elsevier Science Publishers, B.V. (1995) chap 142

(3) G. D. Sandrock and G. Thomas, IEA technical report, compilation of IEA/DOE/SNL hydride database, (1997)

(4) P.D. Goodell, G. D. Sandrock and E.L. Huston, Pept. SAND 79-7095, Sandia N.L. Albuquerque, NM 87185 (1980) pp 1-176

(5) G.D. Sandrock, proc. 12th intersociety energy conversion engineering conference, Am. Nuclear Soc., 1 (1977) 951

(6) G.D. Sandrock, in A.F. Andersen, A.J. Mealand (eds.) Proc. Int. Symp. on Hydrides for Energy Storage 9, Pergamon, Oxford (1979), 1625

(7) G.D. Sandrock, J.J. Murray, M.L. Post and J.B. Taylor, Mat. Res. Bull., 17 (1982) 887

(8) P.D. Goodell, J. Less-Common Met., 99 (1984) 1

CLAIMS

1) An alloy of the general formula:

$$(Ca_c\, Mg_d\, M_e)_b\, (Ni_{1-z}T_z)_a$$

where:

M is at least one metal selected from the group consisting of Y, Ce, La, Pr, Nd, Th, Nd, Ti, V, Zr, Ta, Hf, Sr, Ba and Misch metals;

T is at least one element selected from the group consisting of Al, Zn, Cu, Fe, Co, Mn, Cr, Mo, W, Si, Ga, Ge, In, Sn, Ag, C and B;

a is an integer equal to 2 or 5;

z is a number ranging from 0 to 0.5, and

when a is equal to 2, then b, c, d, e are numbers selected so that:

$0.9 \leq b \leq 1.1$

$c = 0.4-x$,

$d = 0.6-y$, and

$e = x+y$, with

$-0.5 \leq x < 0.4$

$-0.4 < y \leq 0.5$ and

$x+y > 0$;

when a is equal to 5, then b, c, d, e are numbers selected so that

<u>either</u>

$1.75 \leq b \leq 2.25$

$c = 0.4-x$,

$d = 0.6-y$, and

$e = x+y$, with

$-0.4 \leq x \leq 0.2$,

$-0.2 \leq y \leq 0.4$, and

$x+y \geq 0$

or

$0.75 \leq b \leq 1.31$,

$c = 0.6-y$,

$d = x+y$, and

$e = 0.4-x$, with

$-0.6 < x < 0,4$,

$-0.4 < y < 0.6$, and

$0 < x+y \leq 0.5$.

2) An alloy as claimed in claim 1, wherein said alloy is of the formula:

$$(Ca_{0.4-x}Mg_{0.6-y}M_{x+y})_b(Ni_{1-z}T_z)_2$$

where M and T are defined as in claim 1 and

$0.9 \leq b \leq 1.1$,

$-0.5 \leq x < 0.4$,

$-0.4 < y \leq 0.5$,

$x+y > 0$, and

$0 \leq z \leq 0.5$.

3) An alloy as claimed in claim 2, wherein:

$-0.1 \leq x \leq 0.25$ and

$-0.1 \leq y \leq 0.15$.

4) An alloy as claimed in claim 1, wherein said alloy is of the formula:

$$(Ca_{0.4-x}Mg_{0.6-y}M_{x+y})_b(Ni_{1-z}T_z)_5$$

where M and T are defined as claimed in claim 1 and

$1.75 \leq b \leq 2.25$,

$-0.4 \leq x \leq 0.2$,

$-0.2 \leq y \leq 0.4$,

$x+y \geq 0$, and

$0 \leq z \leq 0.5$.

5) An alloy as claimed in claim 4, wherein:

$-0.1 \leq x \leq 0.1$, and

$-0.1 \leq y \leq 0.2$.

6) An alloy as claimed in claim 4 or 5, wherein Mg and Ca are present in a Mg/Ca ratio ranging between 0.5 and 2.

7) An alloy as claimed in claim 6, wherein the Mg/Ca ratio is ranging between 1.5 and 1.75.

8) An alloy as claimed in claim 1, wherein said alloy is of the formula:

$$(Ca_{0.6-y}Mg_{x+y}M_{0.4-x})_b(Ni_{1-z}T_z)_5$$

where M and T are defined as in claim 1 and

$0.75 \leq b \leq 1.31$,

$-0.6 < x < 0.4$,

$-0.4 < y < 0.6$,

$o < x+y \leq 0.5$, and

$0 \leq z \leq 0.5$.

9) An alloy as claimed in claim 8, w herein:

$-0.2 \leq x \leq 0.2$,

$-0.2 \leq y \leq 0.2$, and

$0.1 \leq x + y \leq 0.4$.

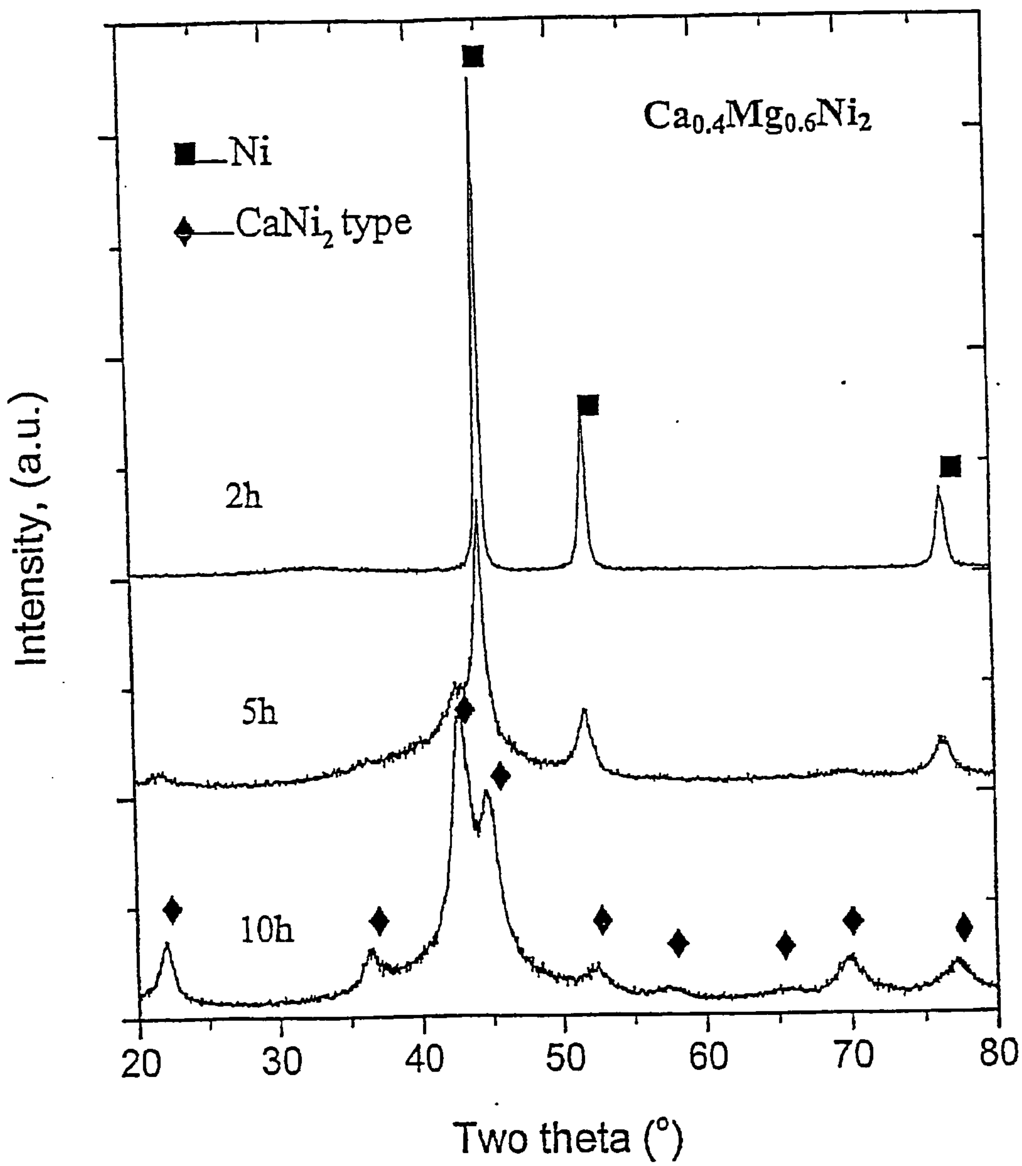
10) An alloy as claimed in any one of claims 1 to 9, wherein said alloy is a single phase alloy.

11) An alloy as claimed in any one of claims 1 to 9, wherein said alloy is a multiphase alloy.

12) A method for preparing an alloy as claimed in any one of claims 1 to 11, comprising the step of:

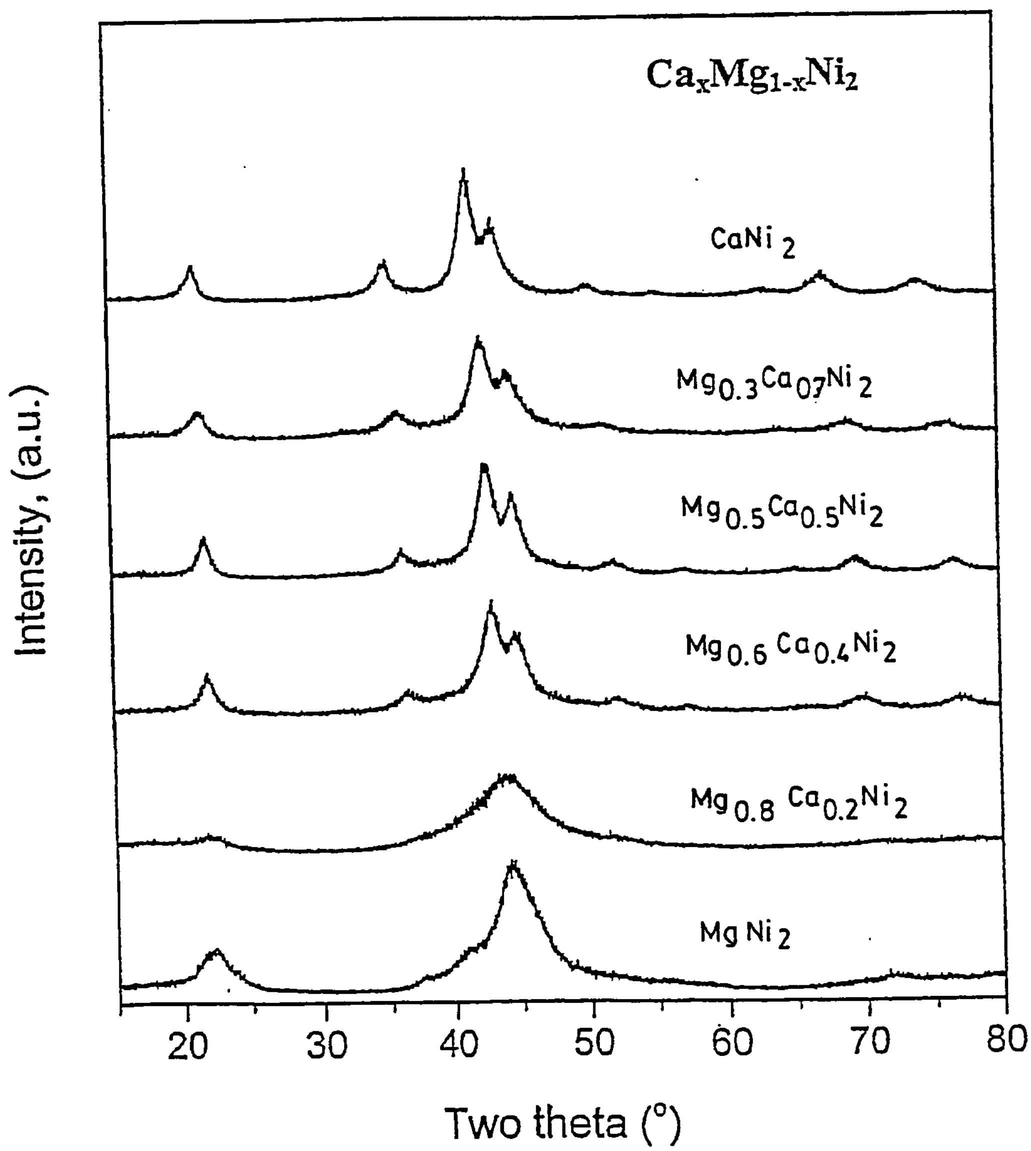
- milling a mixture of elemental powders and/or pre-alloyed combination of elemental powders of Ca, Mg, M, Ni and T in relative amounts corresponding to those found in the requested alloy, and
- annealing and/or sintering the so-milled mixture of powders at a temperature higher than 800°C to obtain the requested alloy.

13) Use of an alloy as claimed in any one of claims 1 to 11 or prepared as claimed in claim 12 for reversibly absorbing hydrogen from a gas phase.



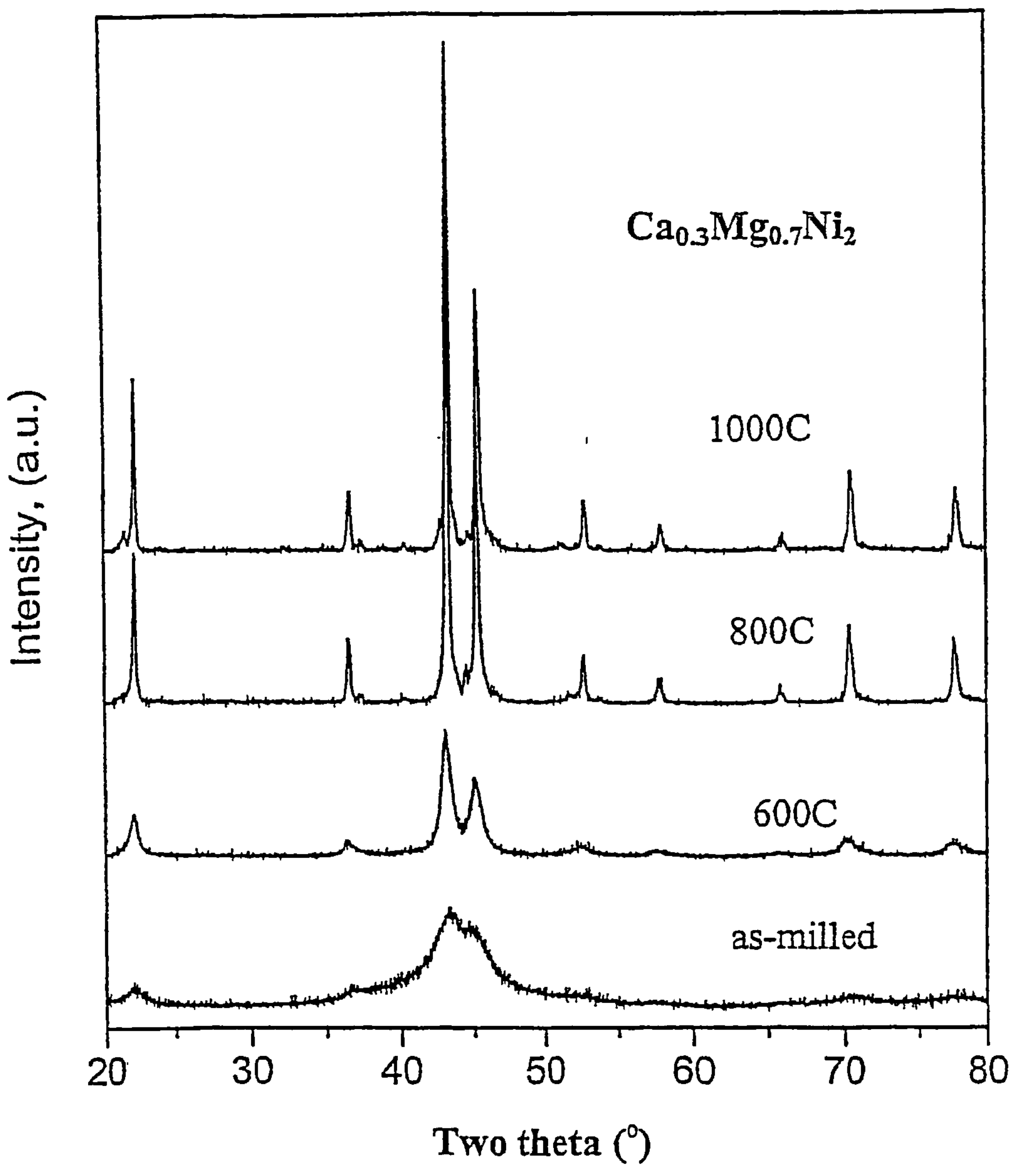
Ca0.4Mg0.6Ni2
Ni
CaNi2 type
2h
5h
10h
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. I-1



$Ca_xMg_{1-x}Ni_2$
$CaNi_2$
$Mg_{0.3}Ca_{07}Ni_2$
$Mg_{0.5}Ca_{0.5}Ni_2$
$Mg_{0.6}Ca_{0.4}Ni_2$
$Mg_{0.8}Ca_{0.2}Ni_2$
$MgNi_2$
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. I-2



$Ca_{0.3}Mg_{0.7}Ni_2$
1000C
800C
600C
as-milled
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. I-3

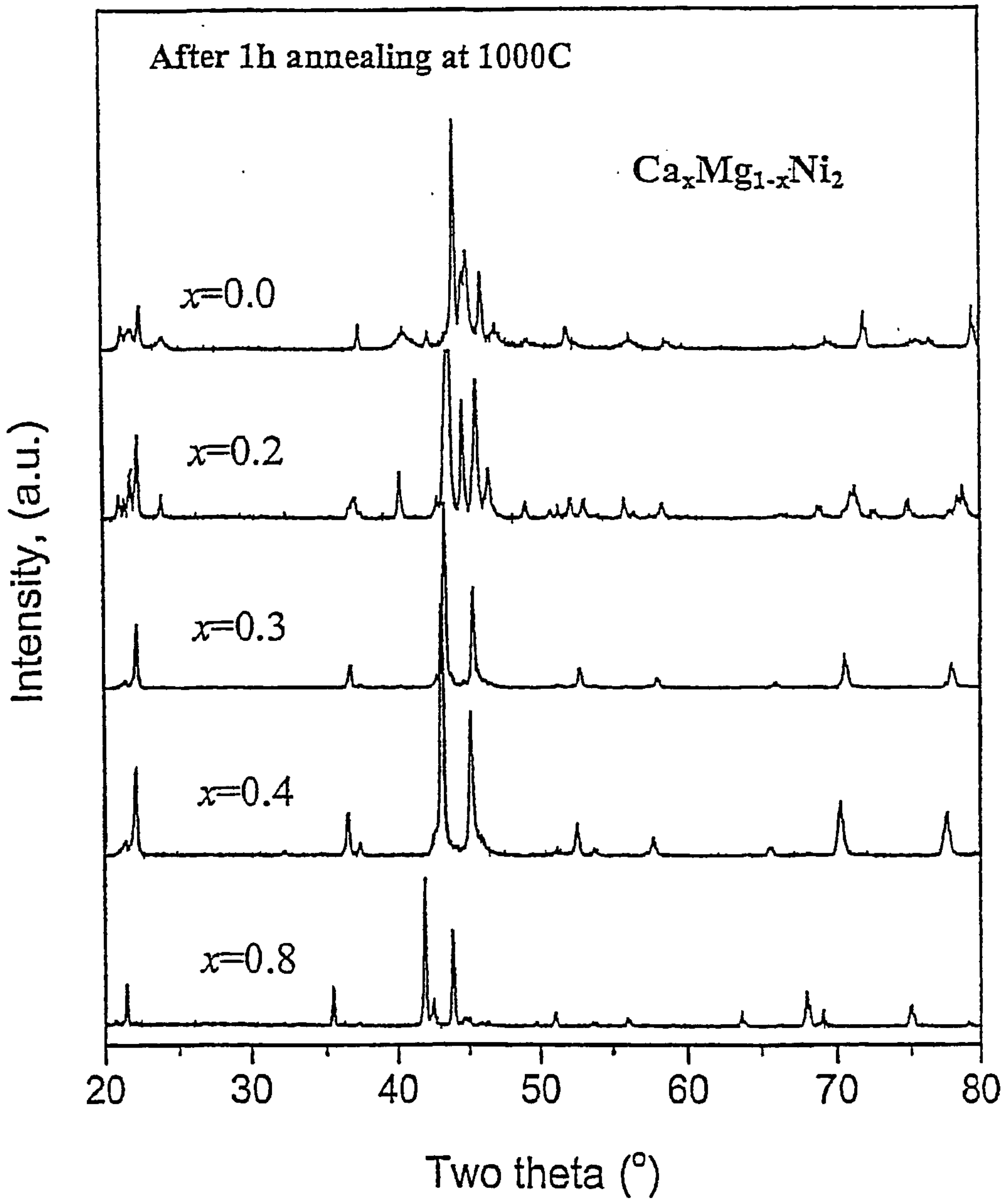
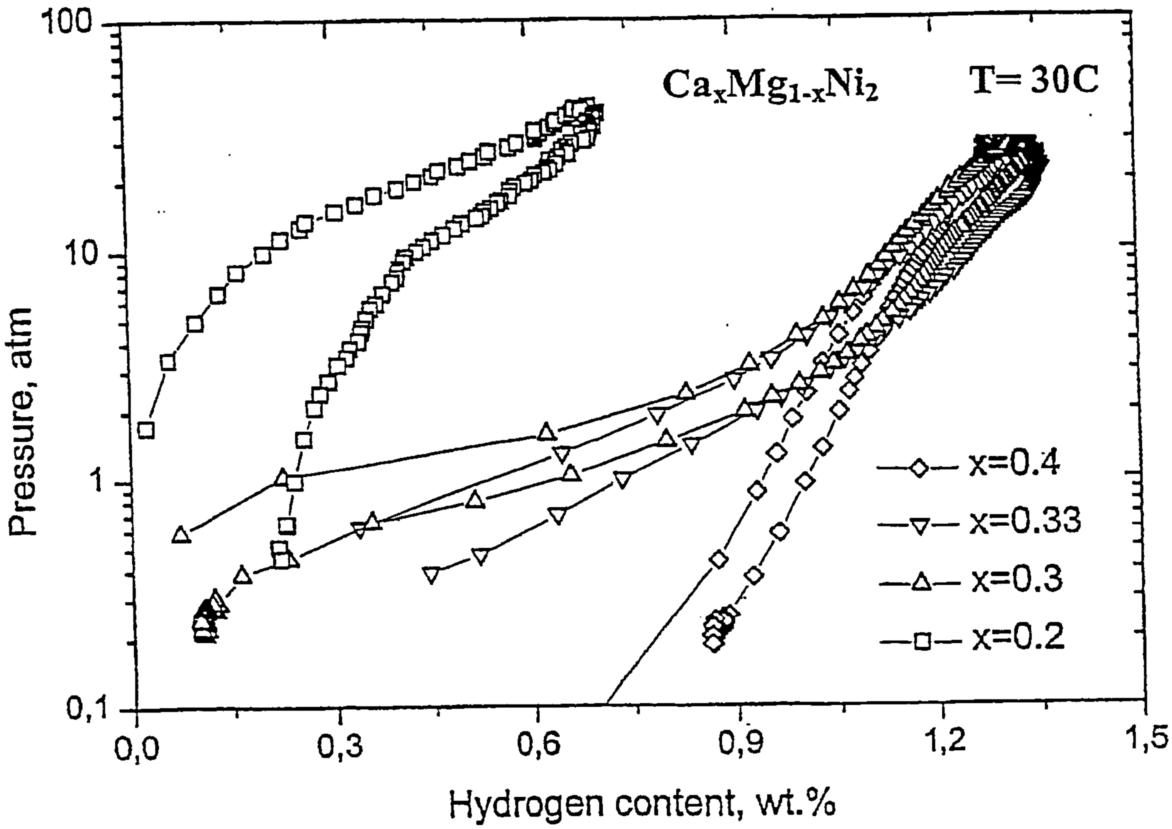

After 1h annealing at 1000C
$Ca_xMg_{1-x}Ni_2$
x=0.0
x=0.2
x=0.3
x=0.4
x=0.8
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. I-4



$Ca_xMg_{1-x}Ni_2$
T= 30C
Pressure, atm
100
10
1
0,1
0,0
0,3
0,6
0,9
1,2
1,5
Hydrogen content, wt.%
x=0.4
x=0.33
x=0.3
x=0.2

FIG. I-5

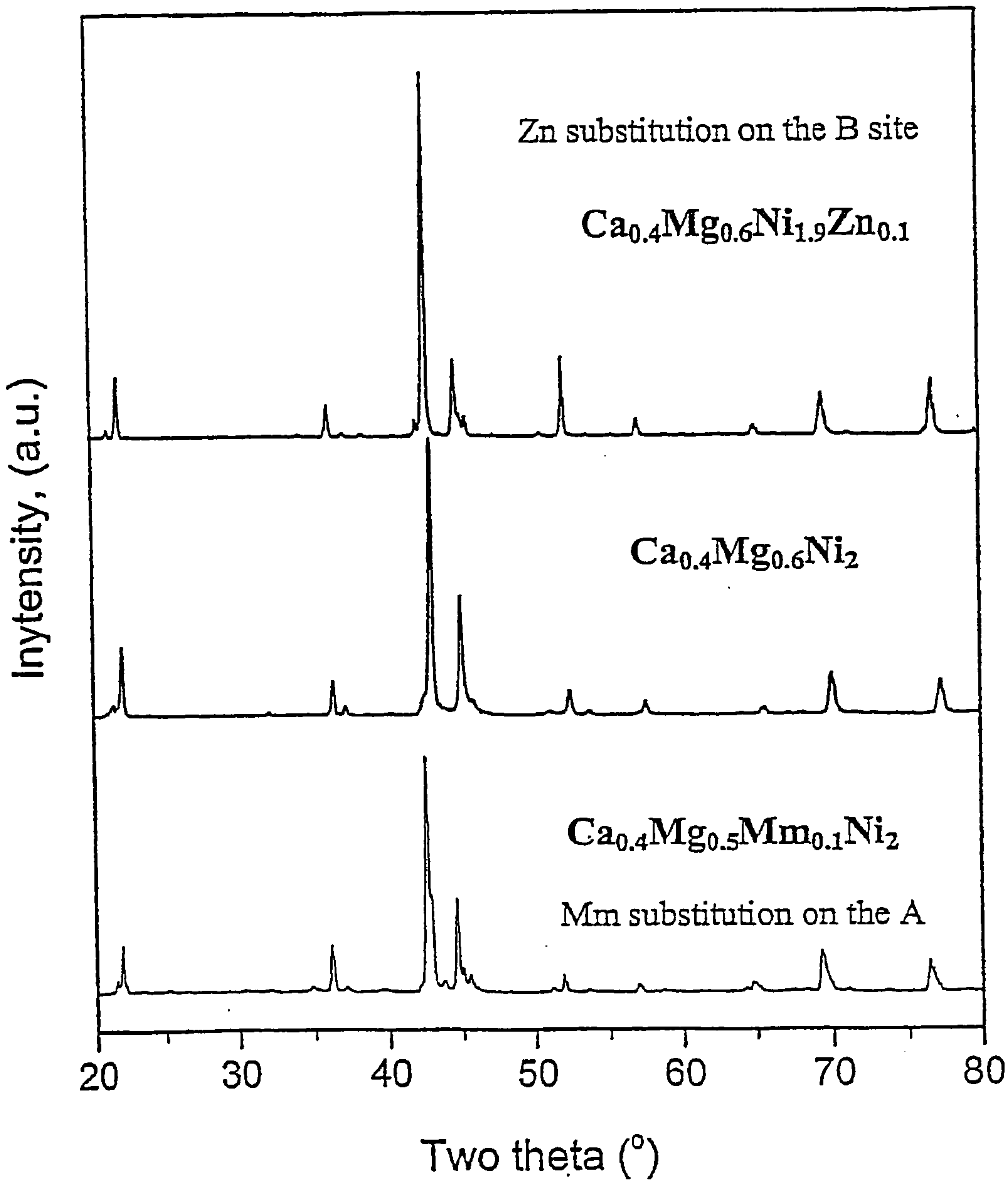

Zn substitution on the B site
$Ca_{0.4}Mg_{0.6}Ni_{1.9}Zn_{0.1}$
$Ca_{0.4}Mg_{0.6}Ni_2$
$Ca_{0.4}Mg_{0.5}Mm_{0.1}Ni_2$
Mm substitution on the A
Inytensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. I-6

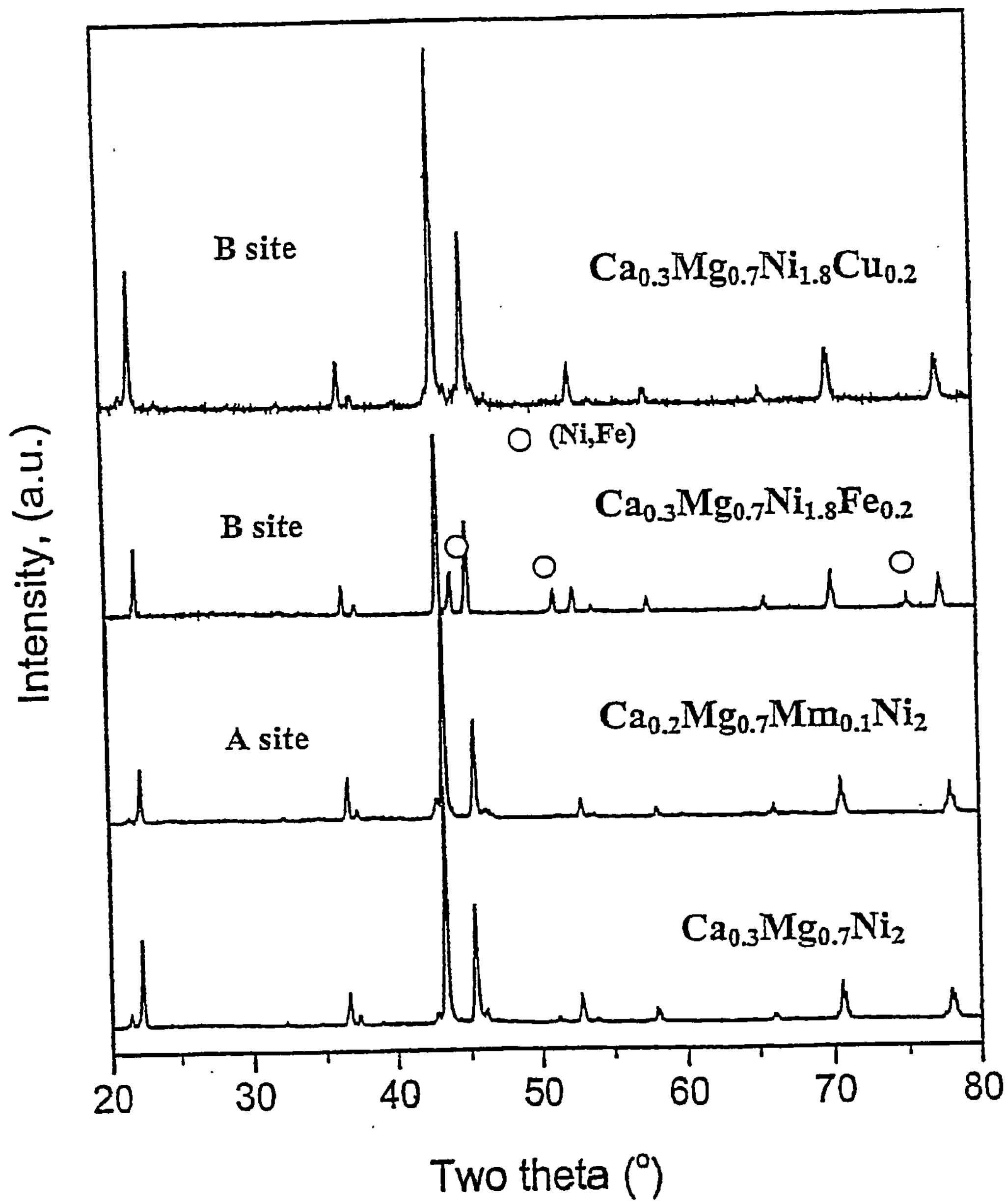
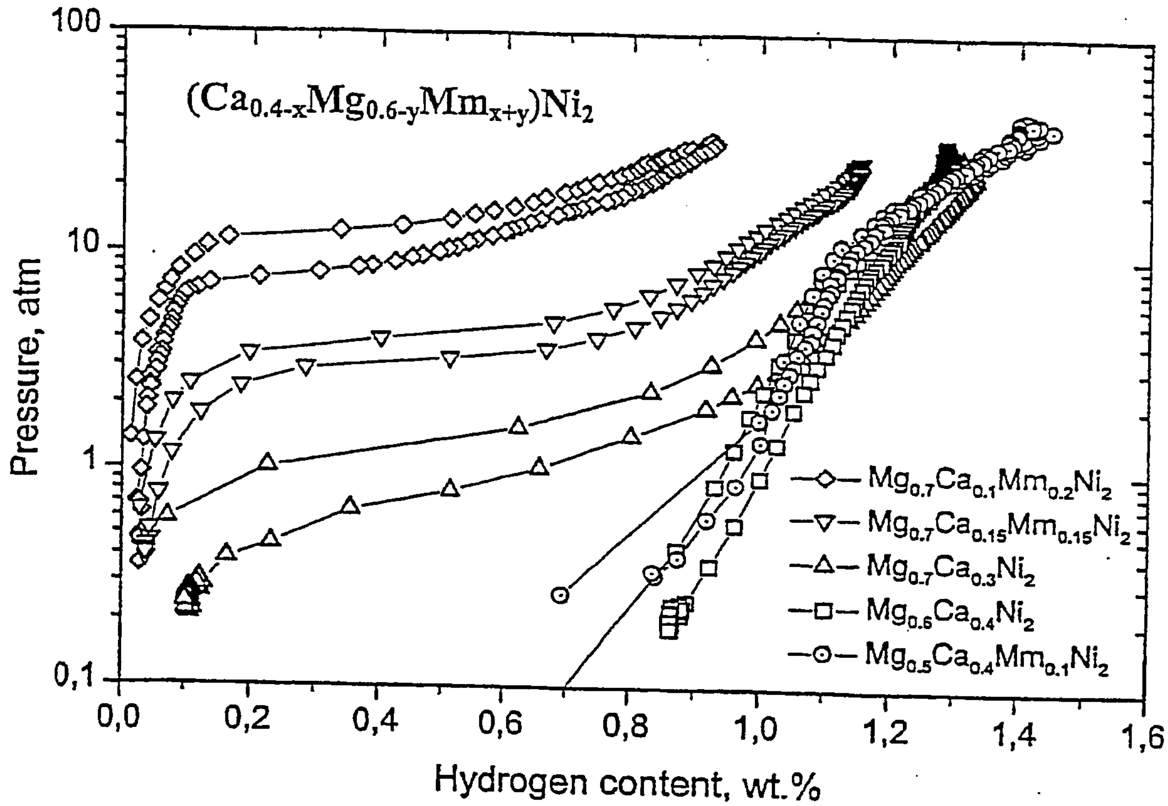

B site
$Ca_{0.3}Mg_{0.7}Ni_{1.8}Cu_{0.2}$
(Ni,Fe)
B site
$Ca_{0.3}Mg_{0.7}Ni_{1.8}Fe_{0.2}$
A site
$Ca_{0.2}Mg_{0.7}Mm_{0.1}Ni_2$
$Ca_{0.3}Mg_{0.7}Ni_2$
Intensity, (a.u.)
20 30 40 50 60 70 80
Two theta (°)

FIG. I-7



(Ca0.4-xMg0.6-yMmx+y)Ni2
Pressure, atm
Hydrogen content, wt.%
100
10
1
0,1
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
Mg0.7Ca0.1Mm0.2Ni2
Mg0.7Ca0.15Mm0.15Ni2
Mg0.7Ca0.3Ni2
Mg0.6Ca0.4Ni2
Mg0.5Ca0.4Mm0.1Ni2

FIG. I-8

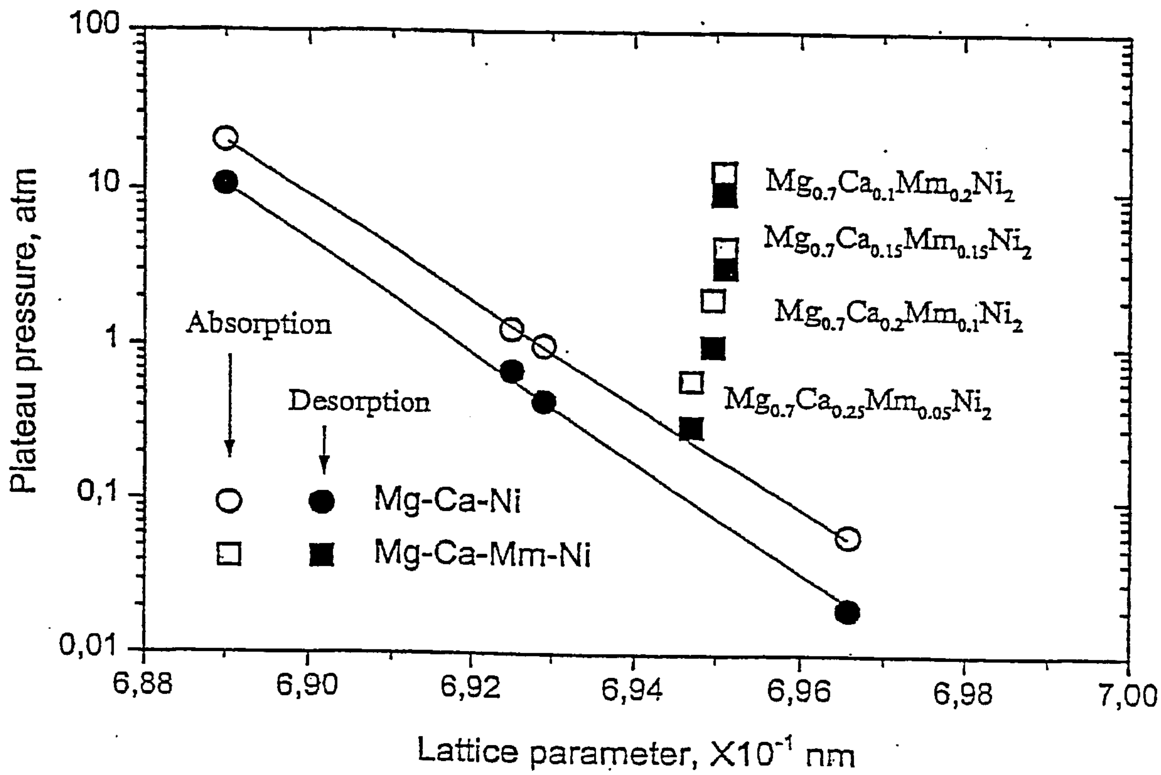
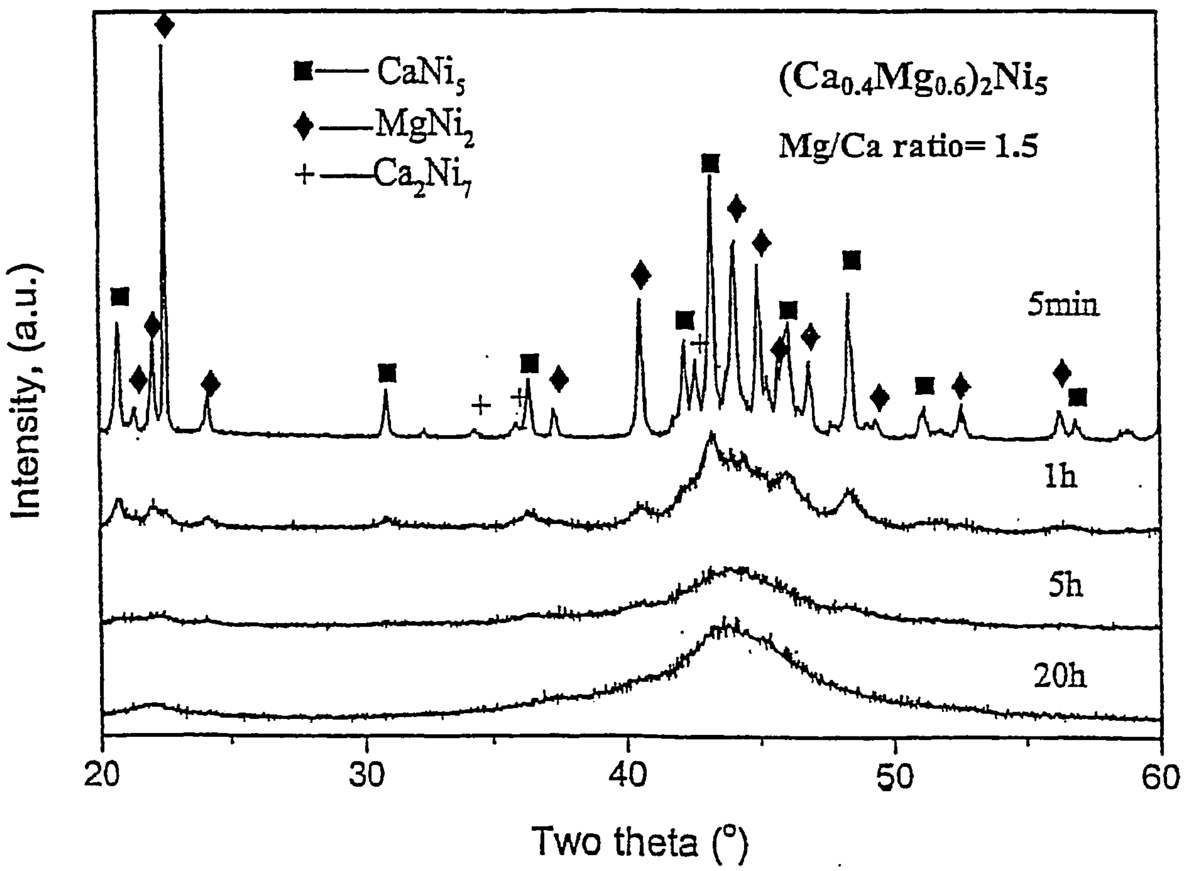

100
10
1
0,1
0,01
Plateau pressure, atm
6,88
6,90
6,92
6,94
6,96
6,98
7,00
Lattice parameter, X10^{-1} nm
Absorption
Desorption
Mg-Ca-Ni
Mg-Ca-Mm-Ni
$Mg_{0.7}Ca_{0.1}Mm_{0.2}Ni_2$
$Mg_{0.7}Ca_{0.15}Mm_{0.15}Ni_2$
$Mg_{0.7}Ca_{0.2}Mm_{0.1}Ni_2$
$Mg_{0.7}Ca_{0.25}Mm_{0.05}Ni_2$

FIG. I-9



■— $CaNi_5$
♦—$MgNi_2$
+—Ca_2Ni_7
$(Ca_{0.4}Mg_{0.6})_2Ni_5$
Mg/Ca ratio= 1.5
5min
1h
5h
20h
Intensity, (a.u.)
20
30
40
50
60
Two theta (°)

FIG. II-1

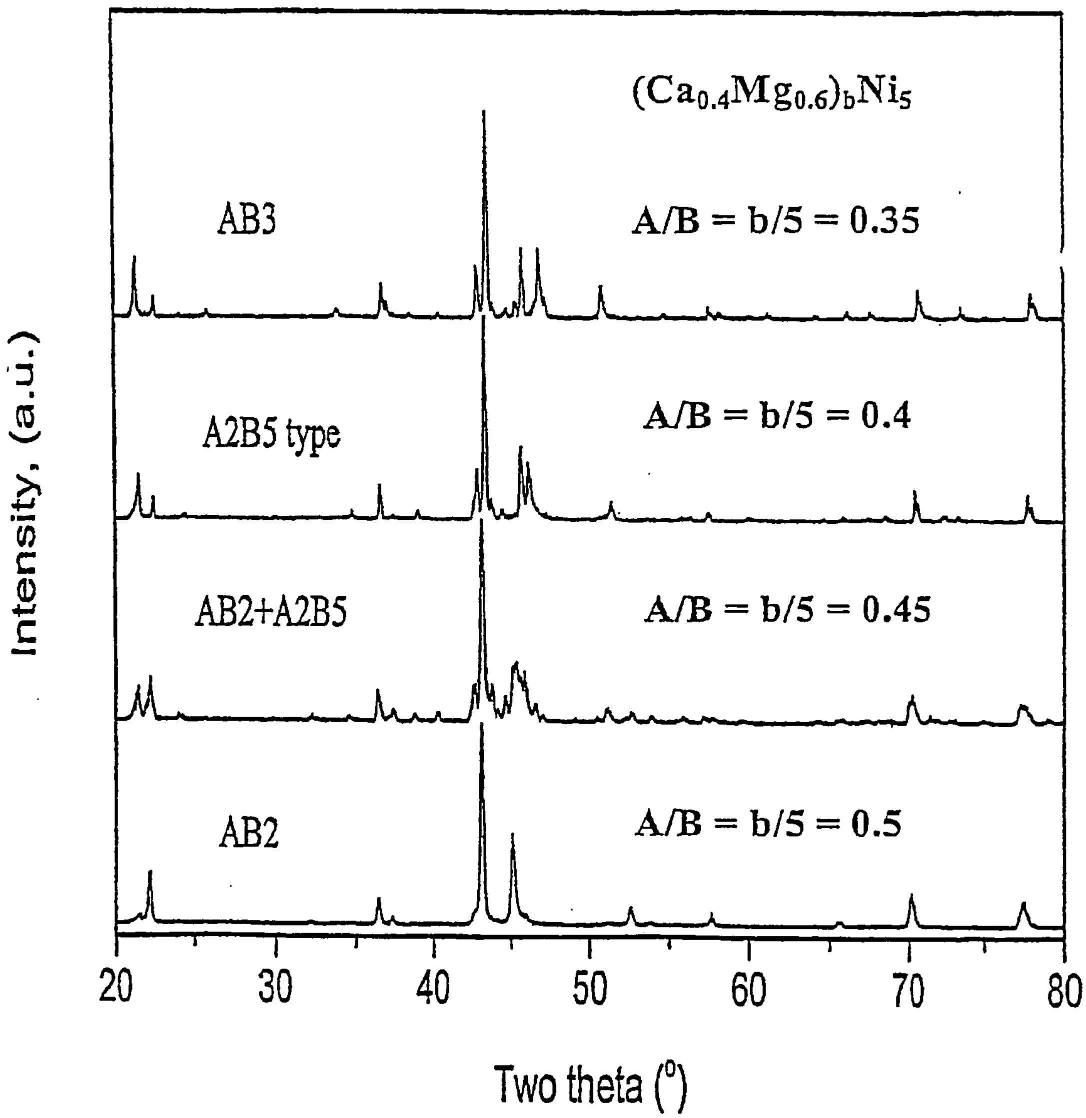
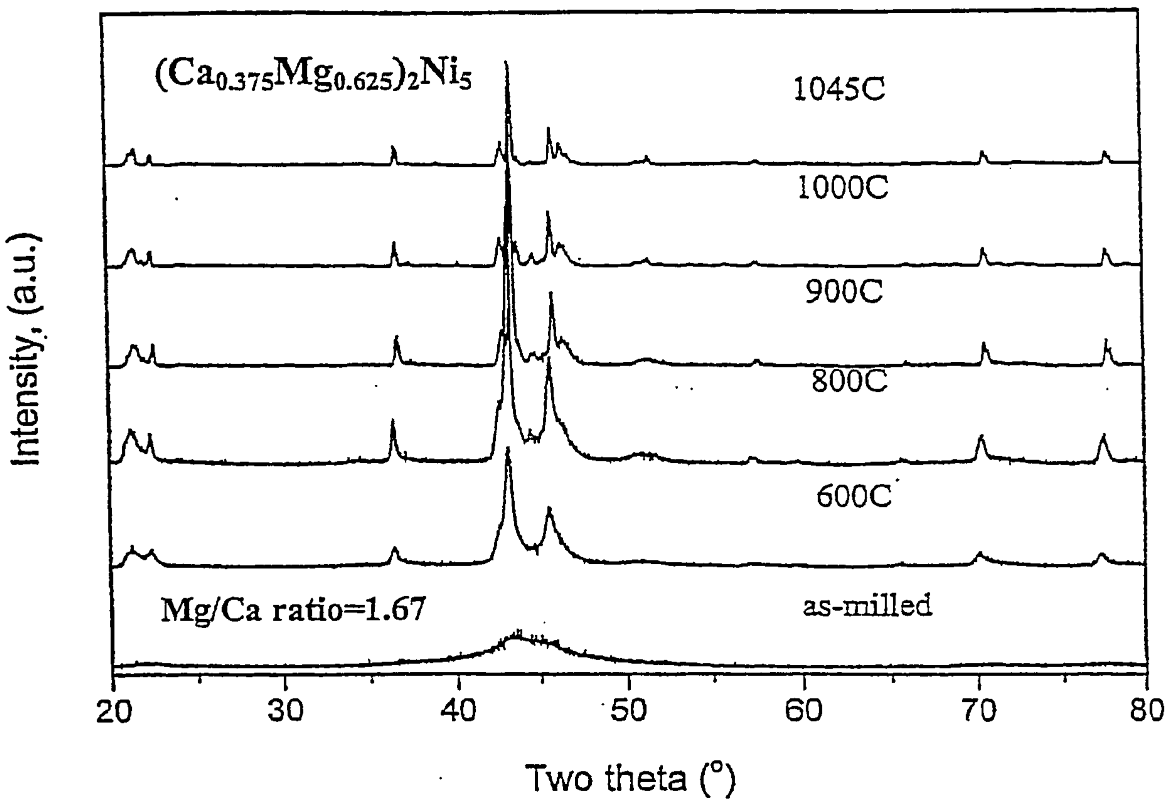
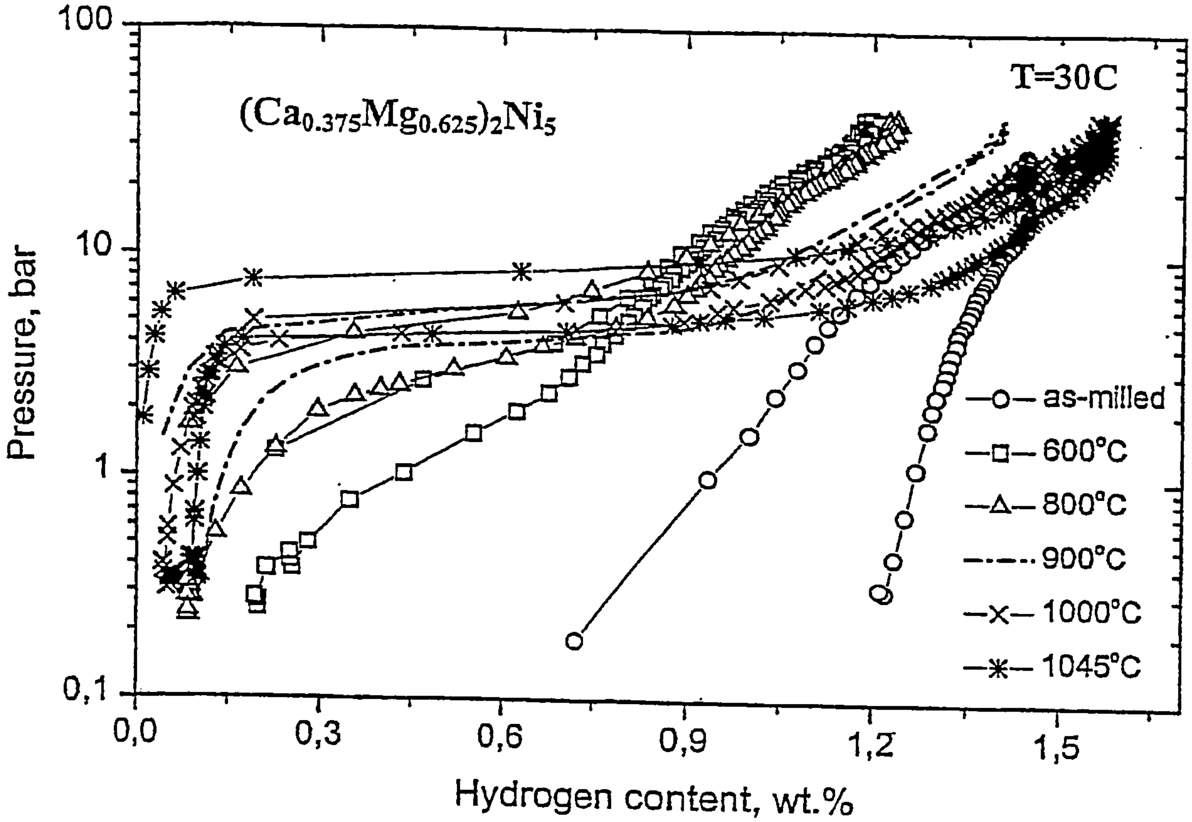

$(Ca_{0.4}Mg_{0.6})_bNi_5$
AB3
A/B = b/5 = 0.35
A2B5 type
A/B = b/5 = 0.4
AB2+A2B5
A/B = b/5 = 0.45
AB2
A/B = b/5 = 0.5
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. II-2



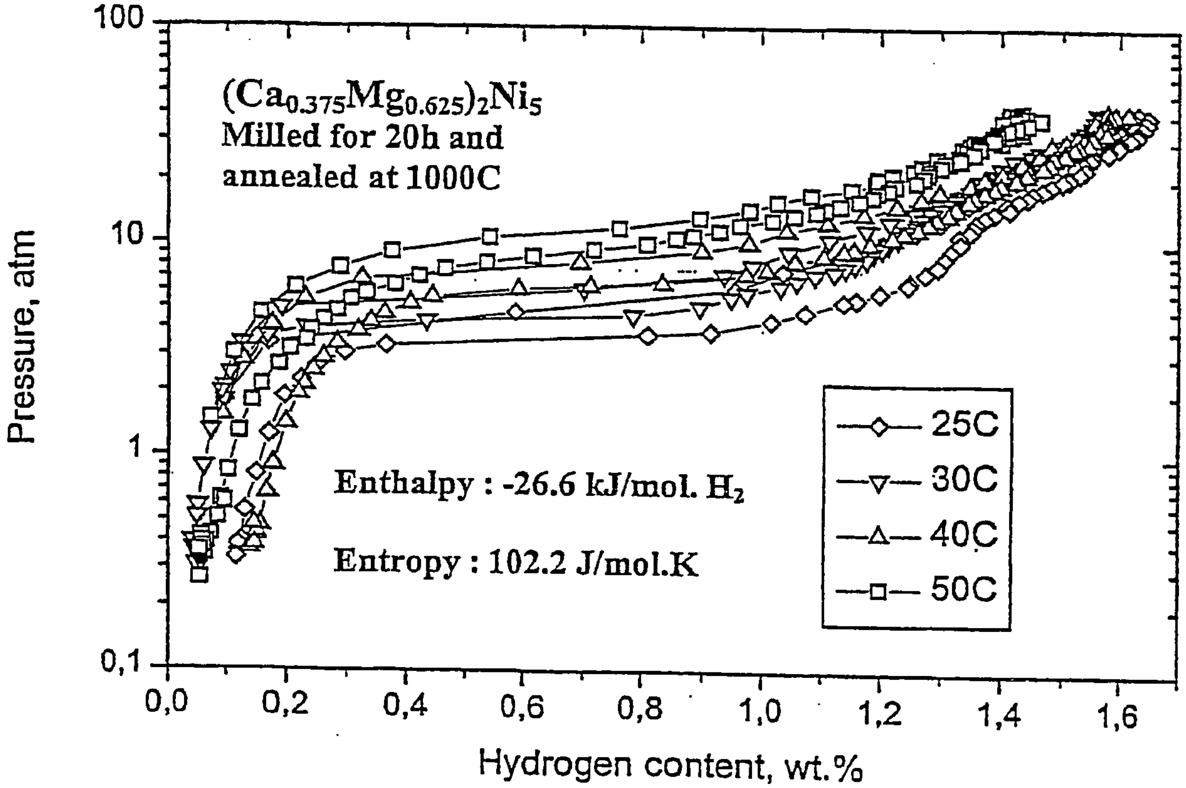
$(Ca_{0.375}Mg_{0.625})_2Ni_5$
1045C
1000C
900C
800C
600C
Mg/Ca ratio=1.67
as-milled
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. II-3



T=30C
(Ca0.375Mg0.625)2Ni5
Pressure, bar
Hydrogen content, wt.%
100
10
1
0,1
0,0
0,3
0,6
0,9
1,2
1,5
as-milled
600°C
800°C
900°C
1000°C
1045°C

FIG. II-4



$(Ca_{0.375}Mg_{0.625})_2Ni_5$
Milled for 20h and
annealed at 1000C
Enthalpy : -26.6 kJ/mol. H_2
Entropy : 102.2 J/mol.K
25C
30C
40C
50C
Pressure, atm
Hydrogen content, wt.%
100
10
1
0,1
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6

FIG. II-5

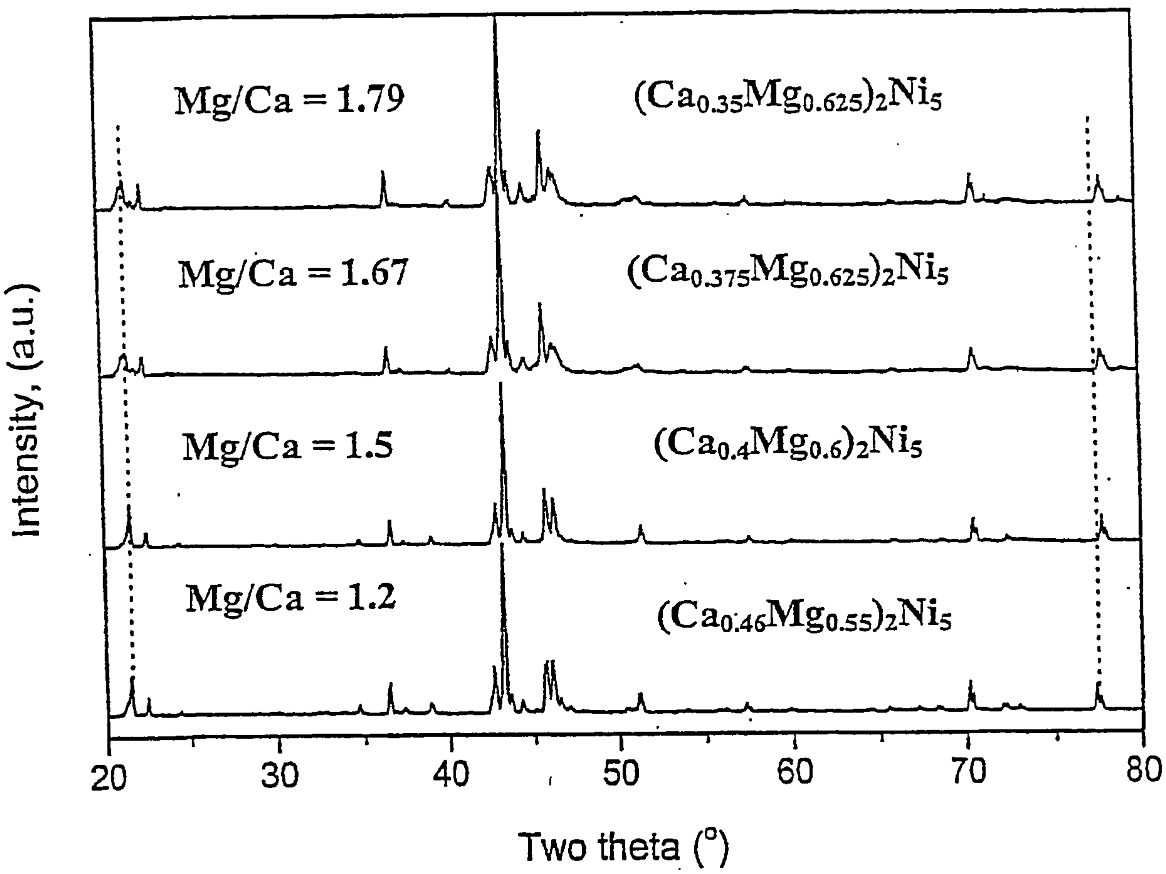
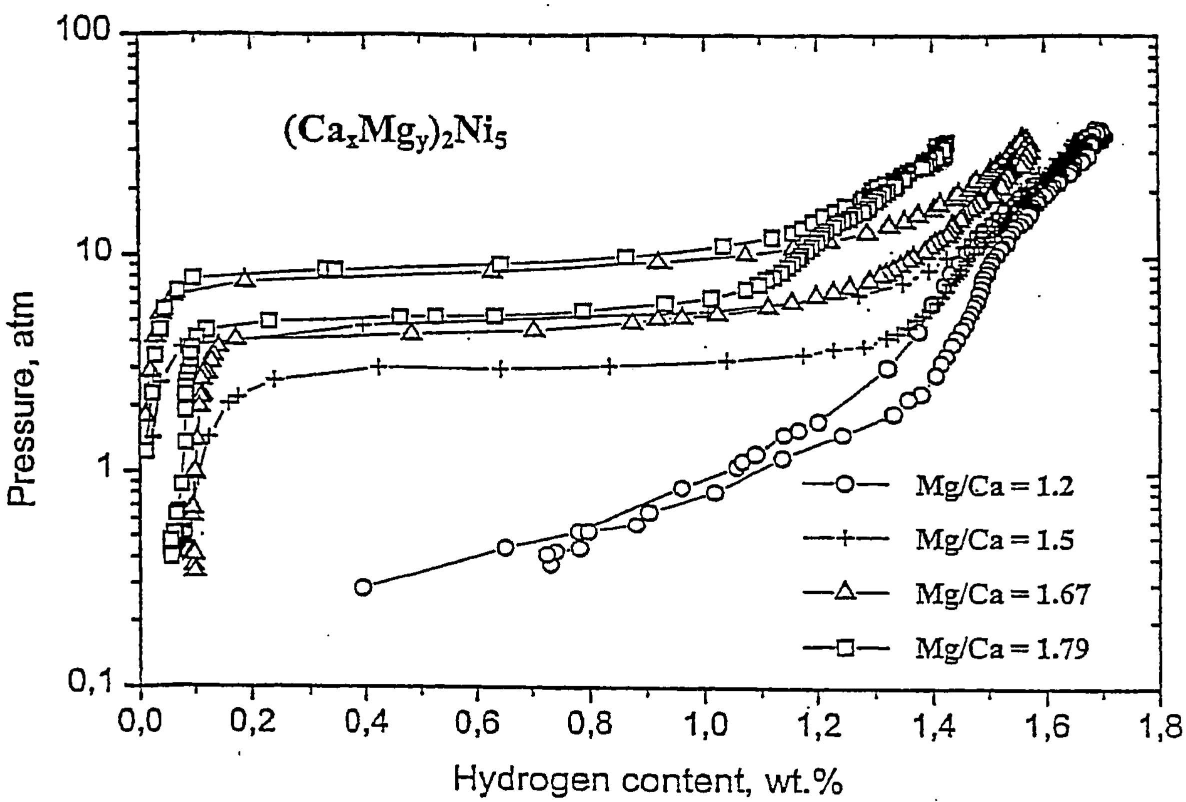

Mg/Ca = 1.79
$(Ca_{0.35}Mg_{0.625})_2Ni_5$
Mg/Ca = 1.67
$(Ca_{0.375}Mg_{0.625})_2Ni_5$
Mg/Ca = 1.5
$(Ca_{0.4}Mg_{0.6})_2Ni_5$
Mg/Ca = 1.2
$(Ca_{0.46}Mg_{0.55})_2Ni_5$
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. II-6



$(Ca_xMg_y)_2Ni_5$
Pressure, atm
100
10
1
0,1
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
1,8
Hydrogen content, wt.%
Mg/Ca = 1.2
Mg/Ca = 1.5
Mg/Ca = 1.67
Mg/Ca = 1.79

FIG. II-7

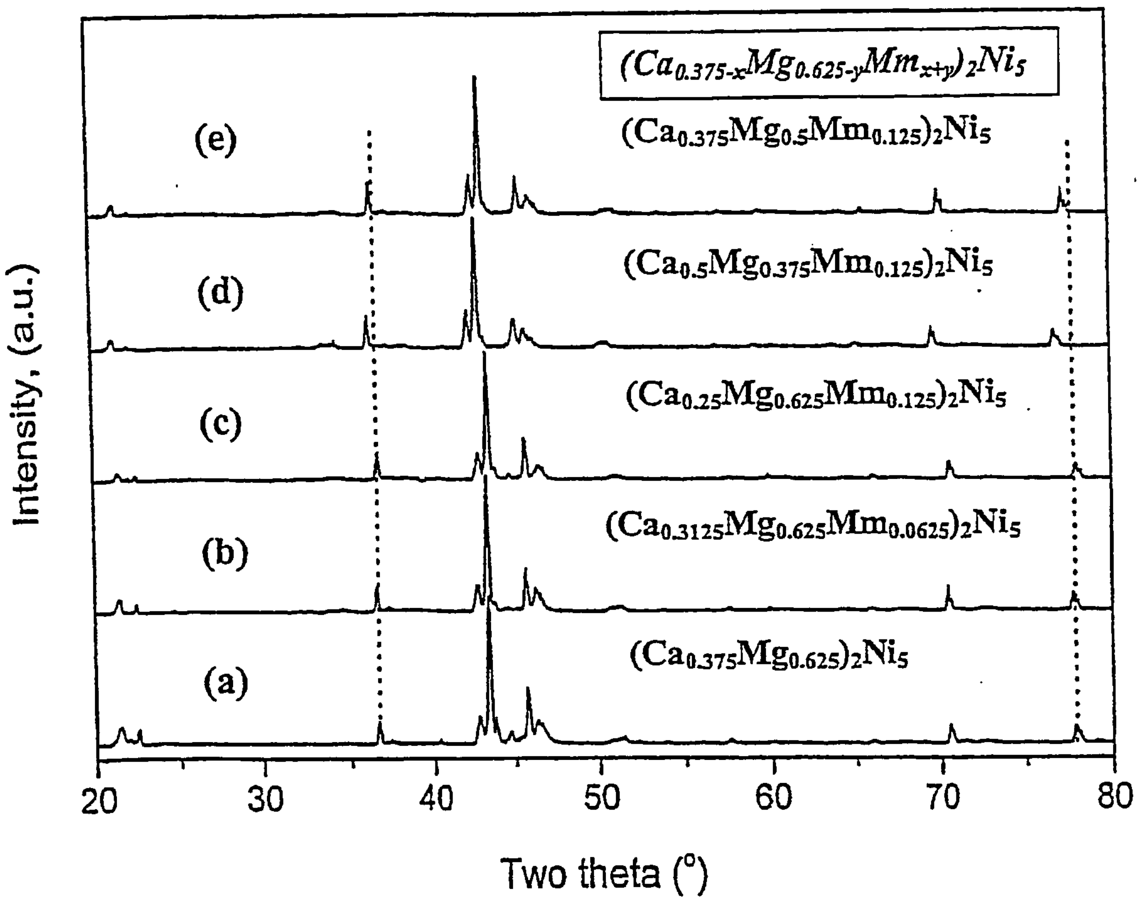
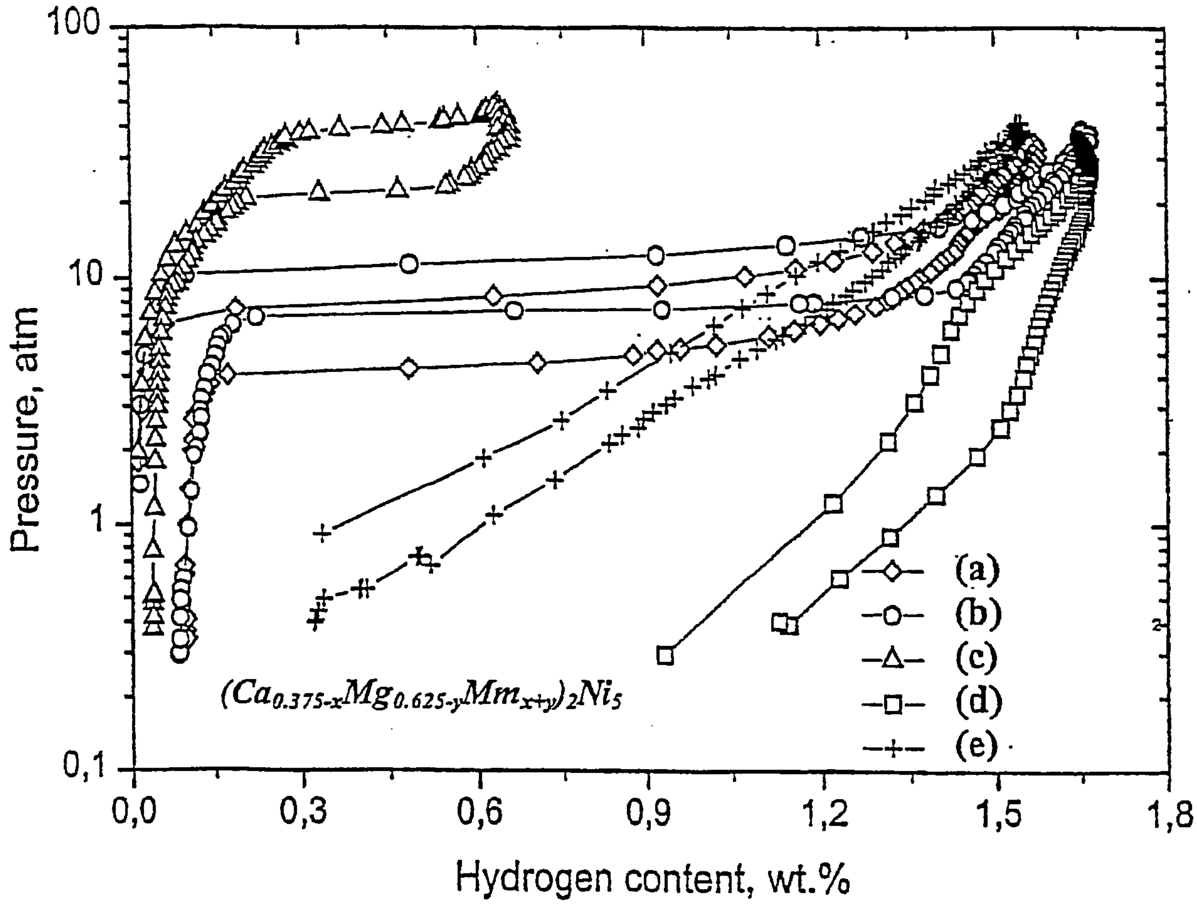


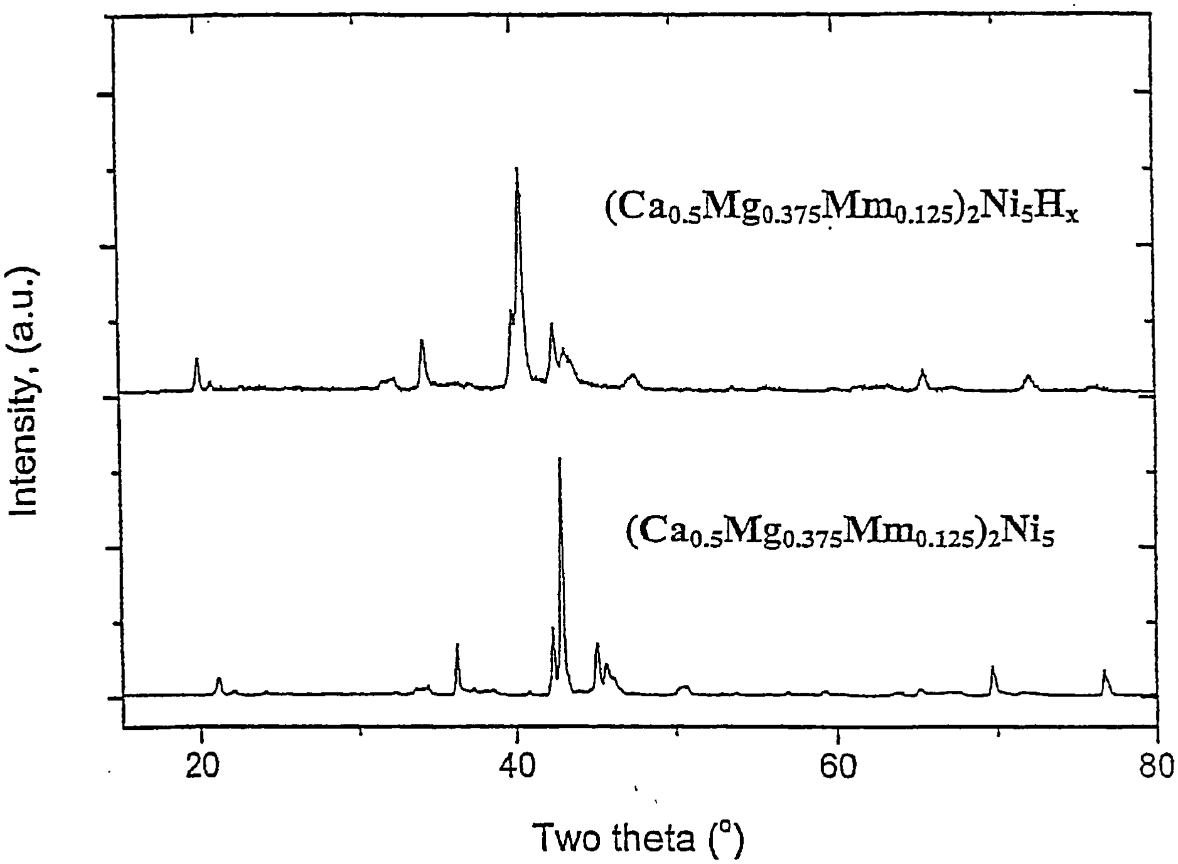
FIG. II-8

SUBSTITUTION ON THE A SITE



100
10
1
0,1
Pressure, atm
0,0
0,3
0,6
0,9
1,2
1,5
1,8
Hydrogen content, wt.%
$(Ca_{0.375-x}Mg_{0.625-y}Mm_{x+y})_2Ni_5$
(a)
(b)
(c)
(d)
(e)

FIG. II-9



$(Ca_{0.5}Mg_{0.375}Mm_{0.125})_2Ni_5H_x$
$(Ca_{0.5}Mg_{0.375}Mm_{0.125})_2Ni_5$
Intensity, (a.u.)
20
40
60
80
Two theta (°)

FIG. II-10

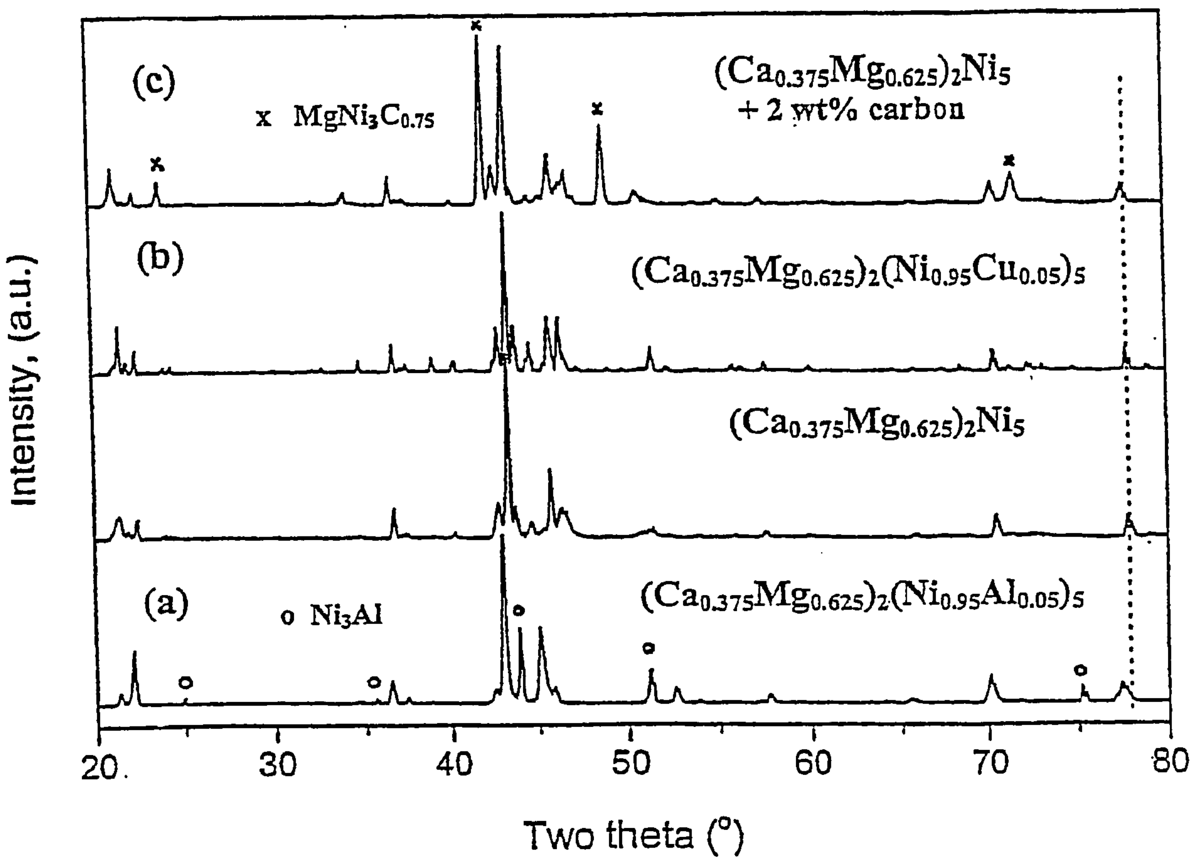
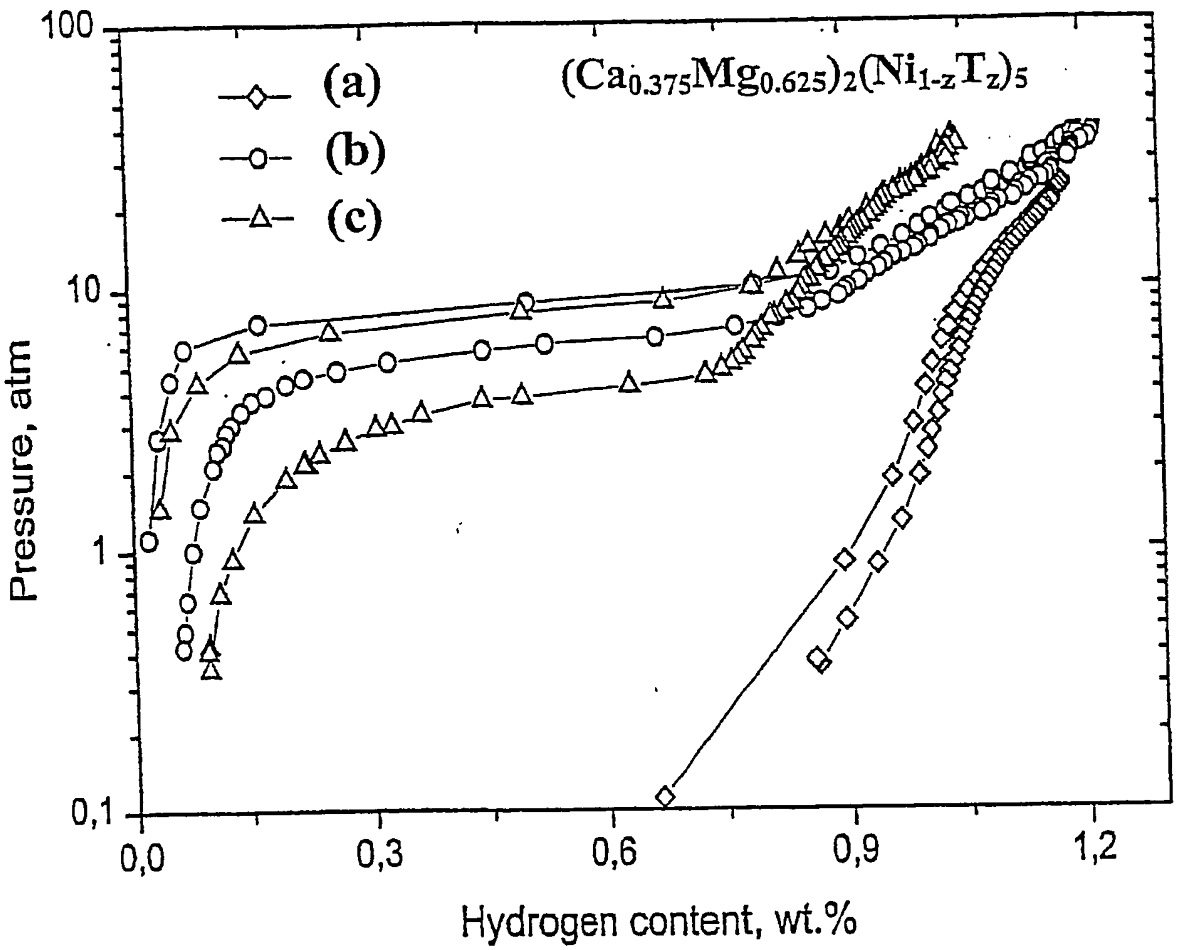


FIG. II-11

SUBSTITUTION ON THE B SITE



100
10
1
0,1
Pressure, atm
(a)
(b)
(c)
$(Ca_{0.375}Mg_{0.625})_2(Ni_{1-z}T_z)_5$
0,0
0,3
0,6
0,9
1,2
Hydrogen content, wt.%

FIG. II-12

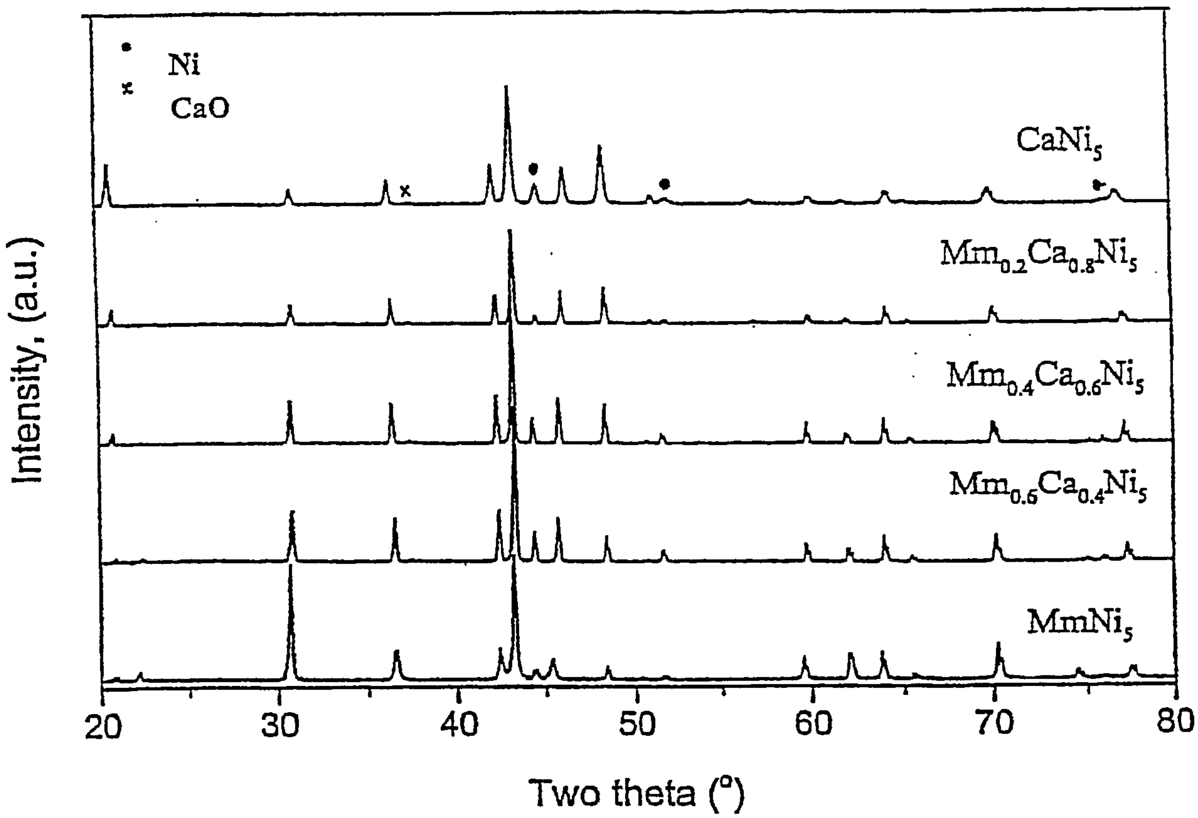
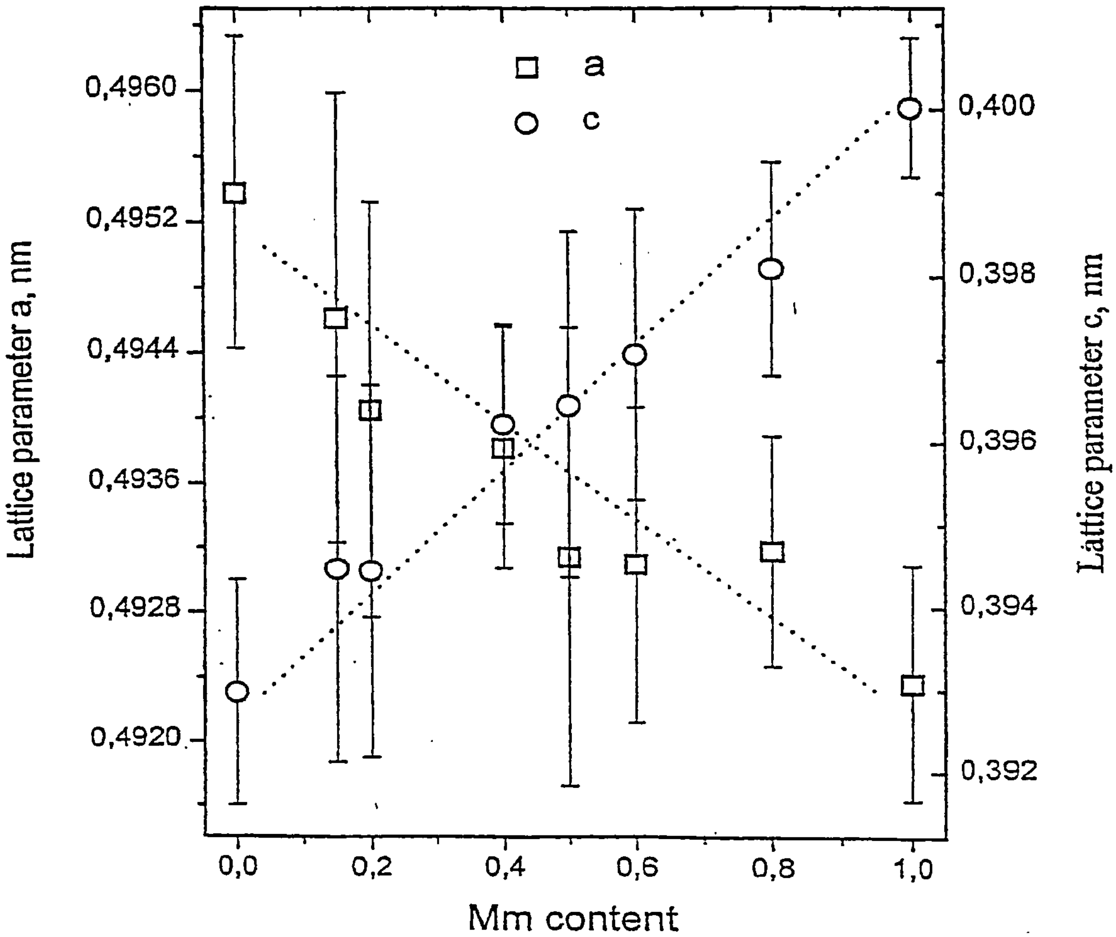
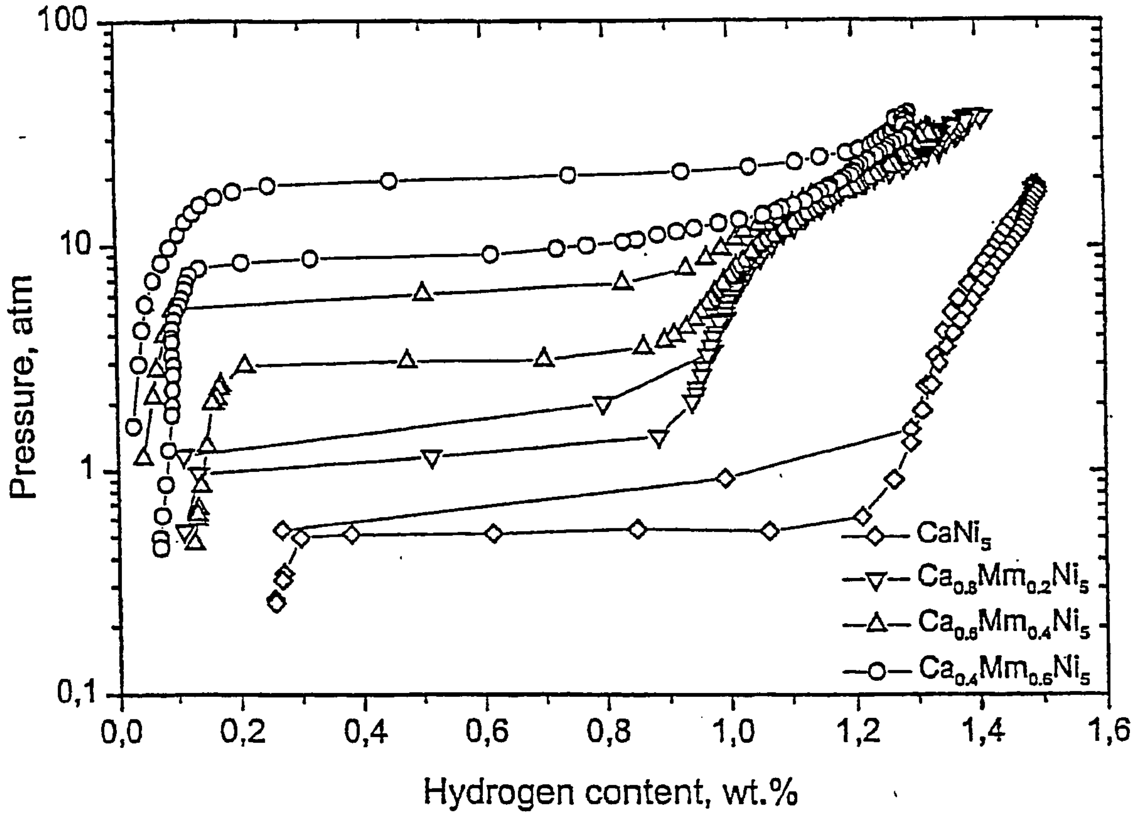

Ni
CaO
CaNi5
Mm0.2Ca0.8Ni5
Mm0.4Ca0.6Ni5
Mm0.6Ca0.4Ni5
MmNi5
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. III-1



a
c
0,4960
0,4952
0,4944
0,4936
0,4928
0,4920
Lattice parameter a, nm
0,400
0,398
0,396
0,394
0,392
Lattice parameter c, nm
0,0
0,2
0,4
0,6
0,8
1,0
Mm content

FIG. III-2



100
10
1
0,1
Pressure, atm
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
Hydrogen content, wt.%
$CaNi_5$
$Ca_{0.8}Mm_{0.2}Ni_5$
$Ca_{0.6}Mm_{0.4}Ni_5$
$Ca_{0.4}Mm_{0.6}Ni_5$

FIG. III-3

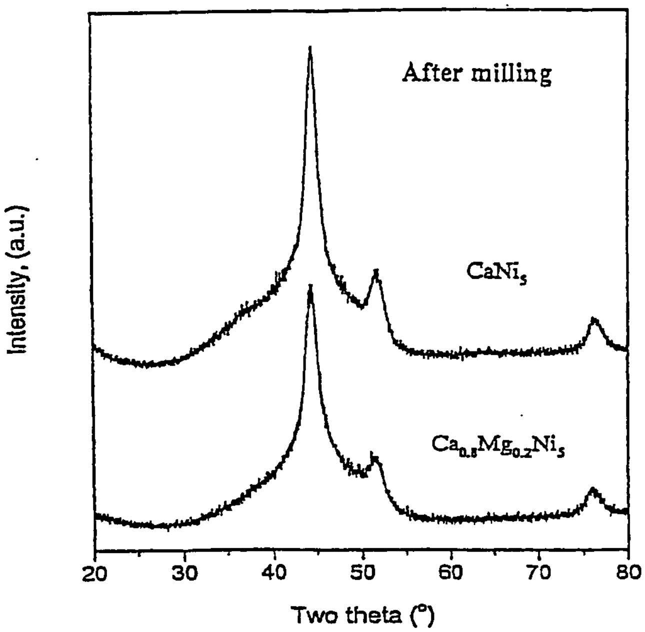


FIG. III-4a

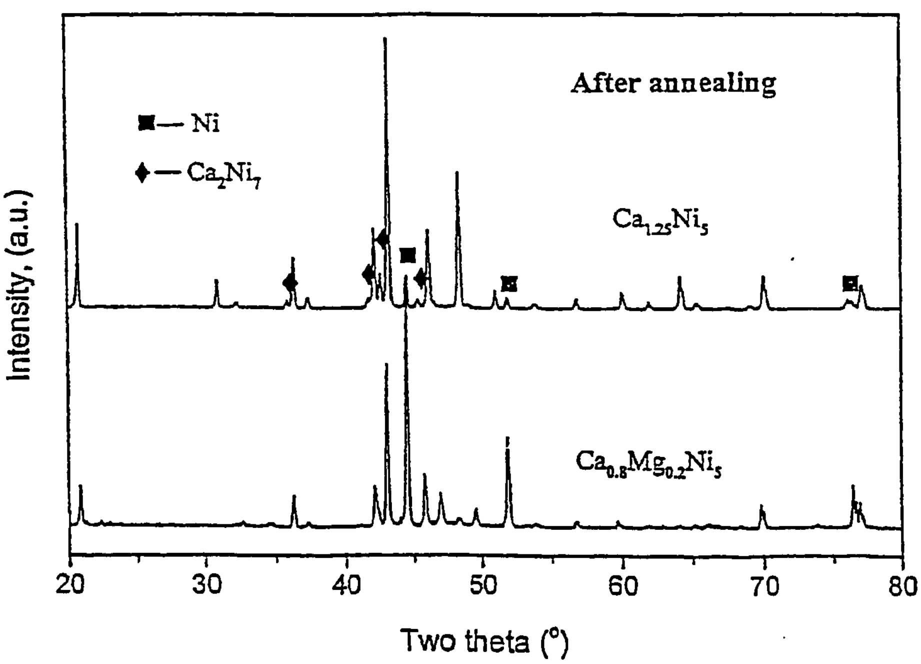


FIG. III-4b

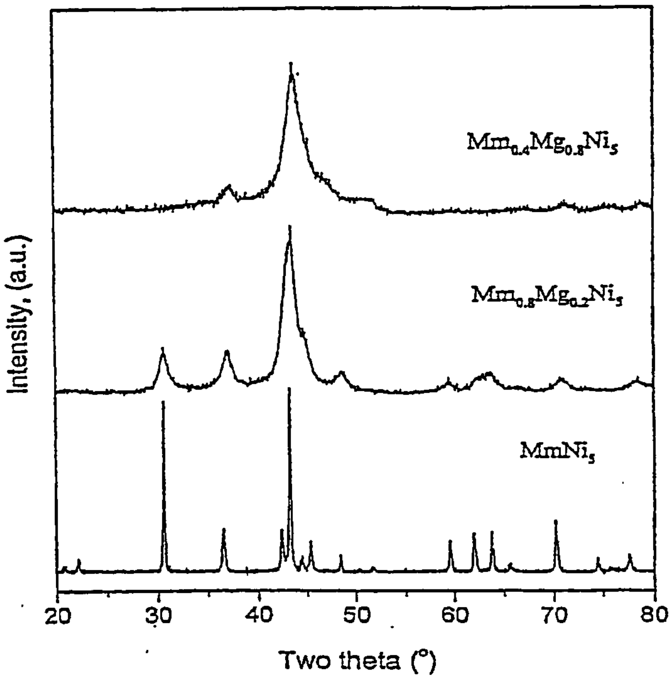


FIG. III-5a

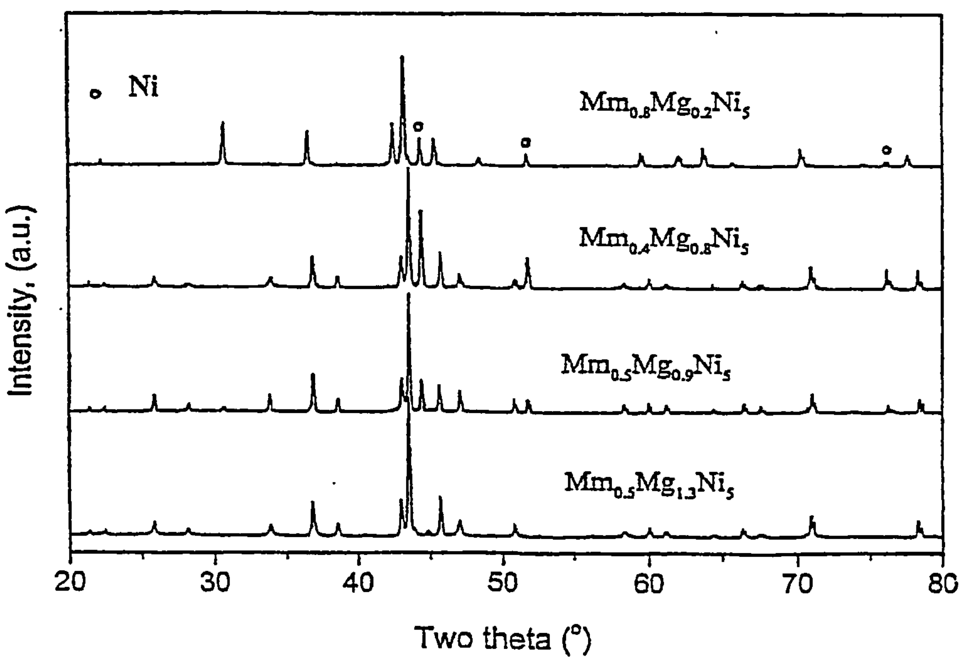
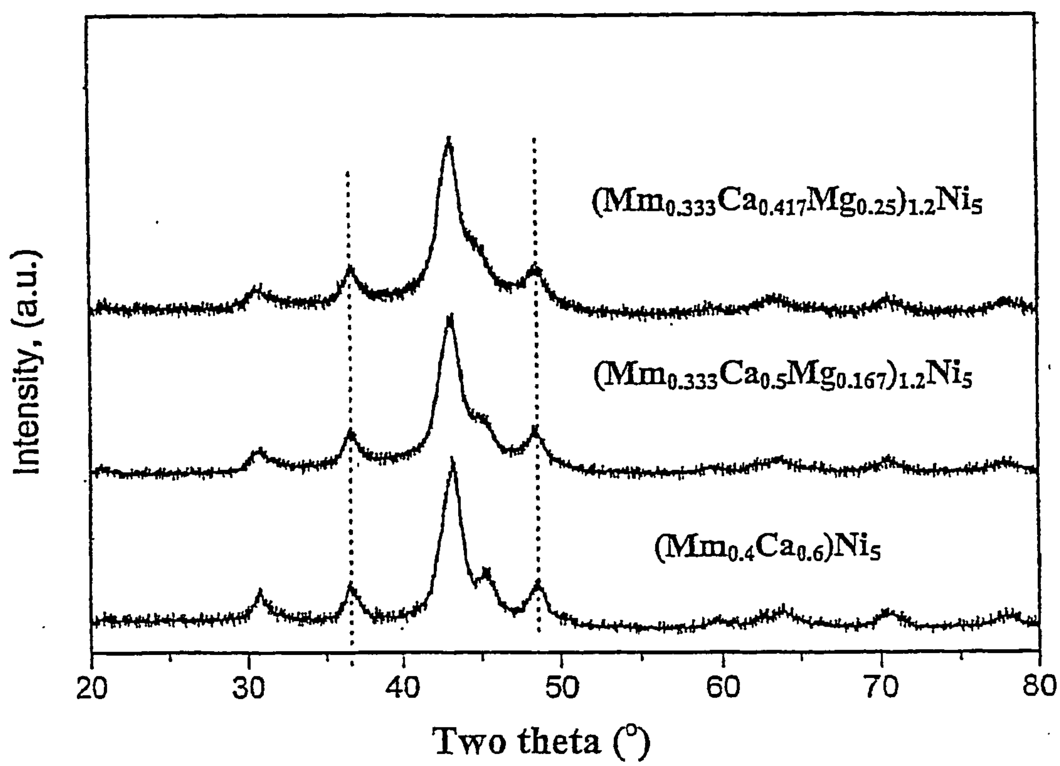
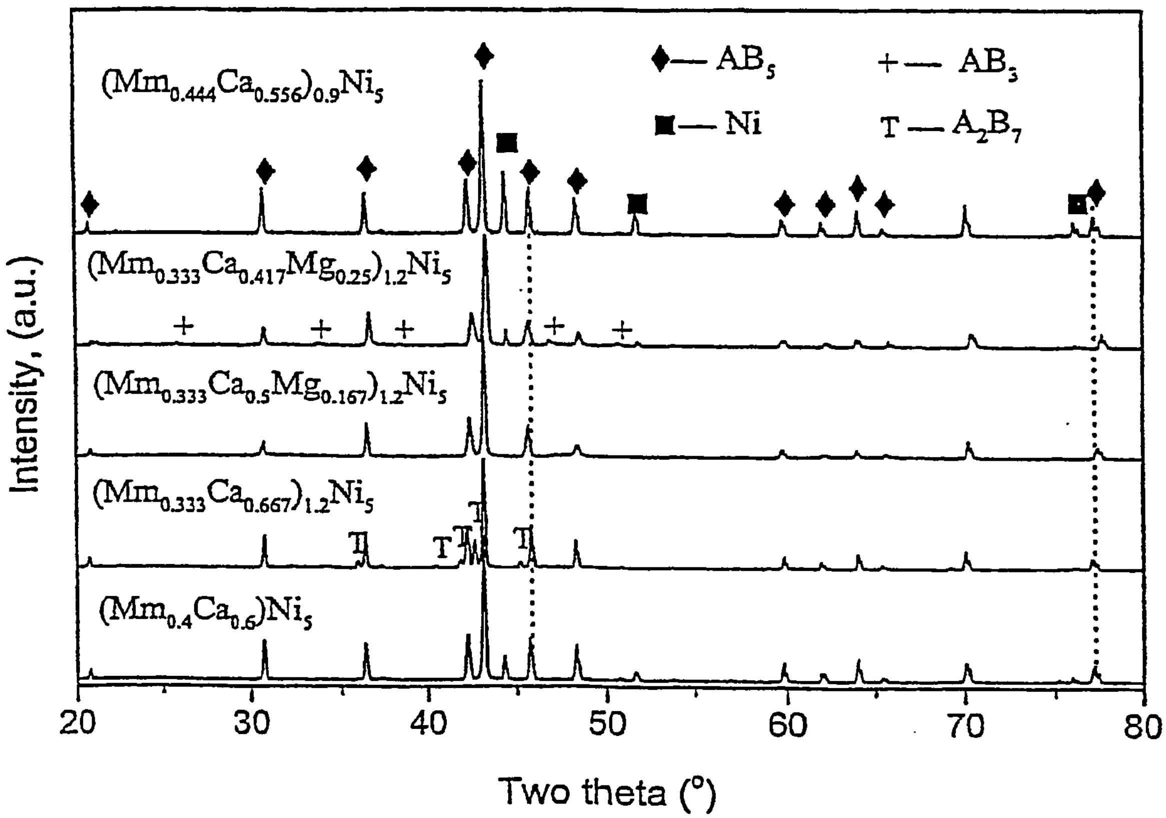


FIG. III-5b



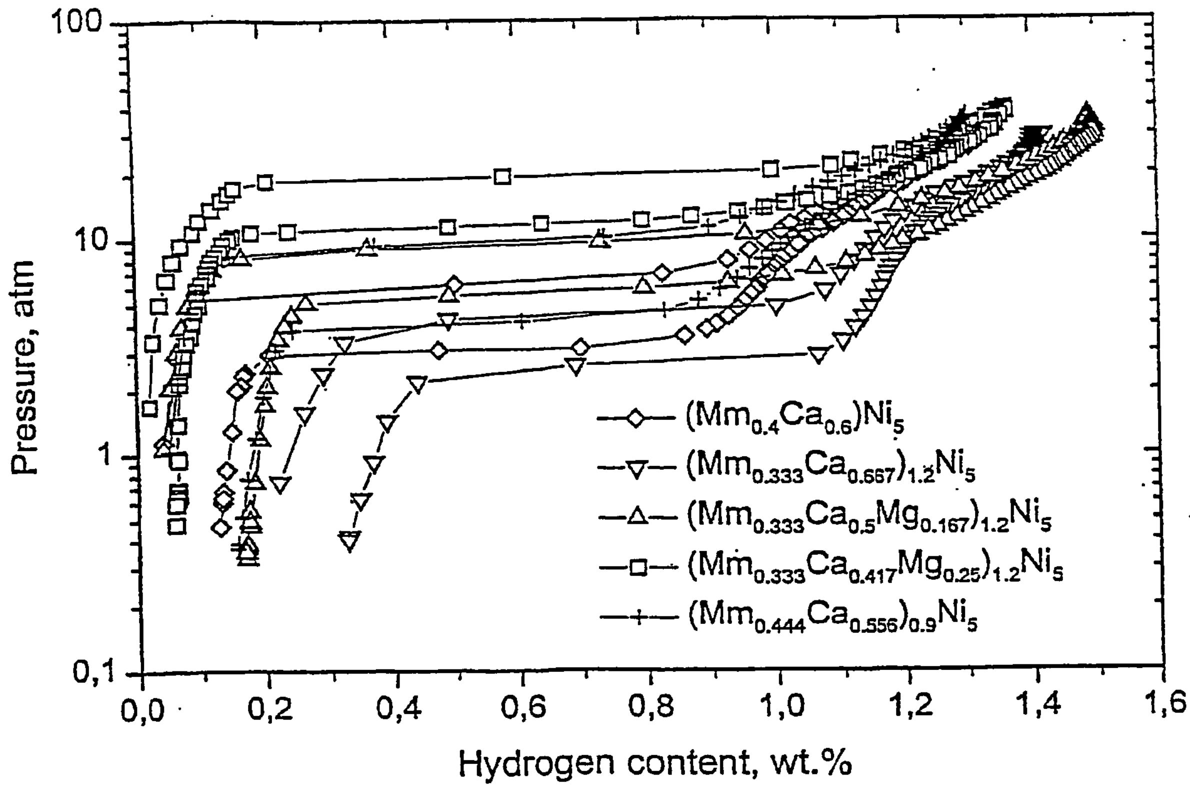
$(Mm_{0.333}Ca_{0.417}Mg_{0.25})_{1.2}Ni_5$
$(Mm_{0.333}Ca_{0.5}Mg_{0.167})_{1.2}Ni_5$
$(Mm_{0.4}Ca_{0.6})Ni_5$
Intensity, (a.u.)
20
30
40
50
60
70
80
Two theta (°)

FIG. III-6



$(Mm_{0.444}Ca_{0.556})_{0.9}Ni_5$
$(Mm_{0.333}Ca_{0.417}Mg_{0.25})_{1.2}Ni_5$
$(Mm_{0.333}Ca_{0.5}Mg_{0.167})_{1.2}Ni_5$
$(Mm_{0.333}Ca_{0.667})_{1.2}Ni_5$
$(Mm_{0.4}Ca_{0.6})Ni_5$
◆— AB_5
+— AB_3
■— Ni
T — A_2B_7
Intensity, (a.u.)
Two theta (°)
20
30
40
50
60
70
80

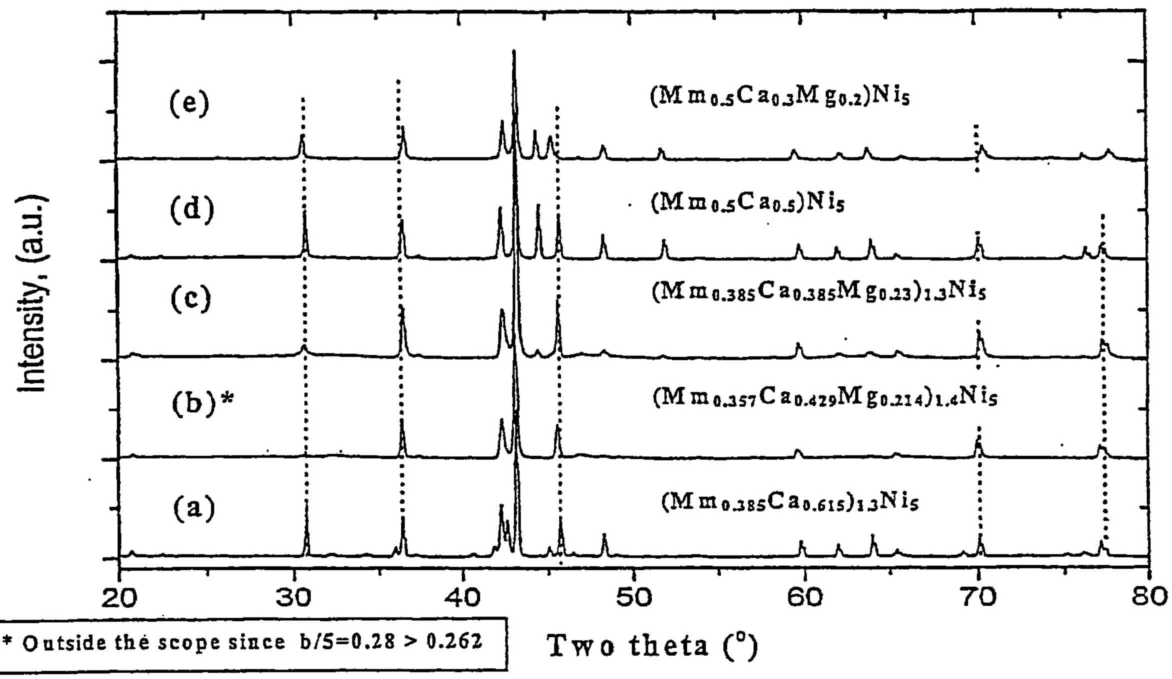
FIG. III-7



100
10
1
0,1
Pressure, atm
0,0
0,2
0,4
0,6
0,8
1,0
1,2
1,4
1,6
Hydrogen content, wt.%
$(Mm_{0.4}Ca_{0.6})Ni_5$
$(Mm_{0.333}Ca_{0.667})_{1.2}Ni_5$
$(Mm_{0.333}Ca_{0.5}Mg_{0.167})_{1.2}Ni_5$
$(Mm_{0.333}Ca_{0.417}Mg_{0.25})_{1.2}Ni_5$
$(Mm_{0.444}Ca_{0.556})_{0.9}Ni_5$

FIG. III-8

FIG. III-9a



* Outside the scope since b/5=0.28 > 0.262

FIG. III-9b

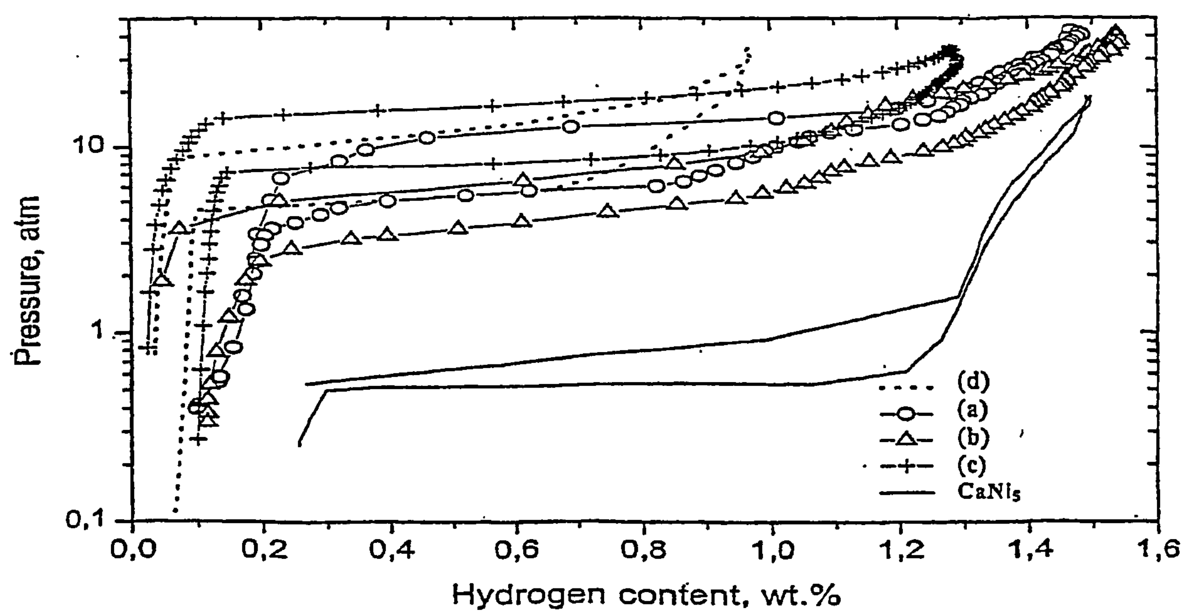


FIG. III-10a

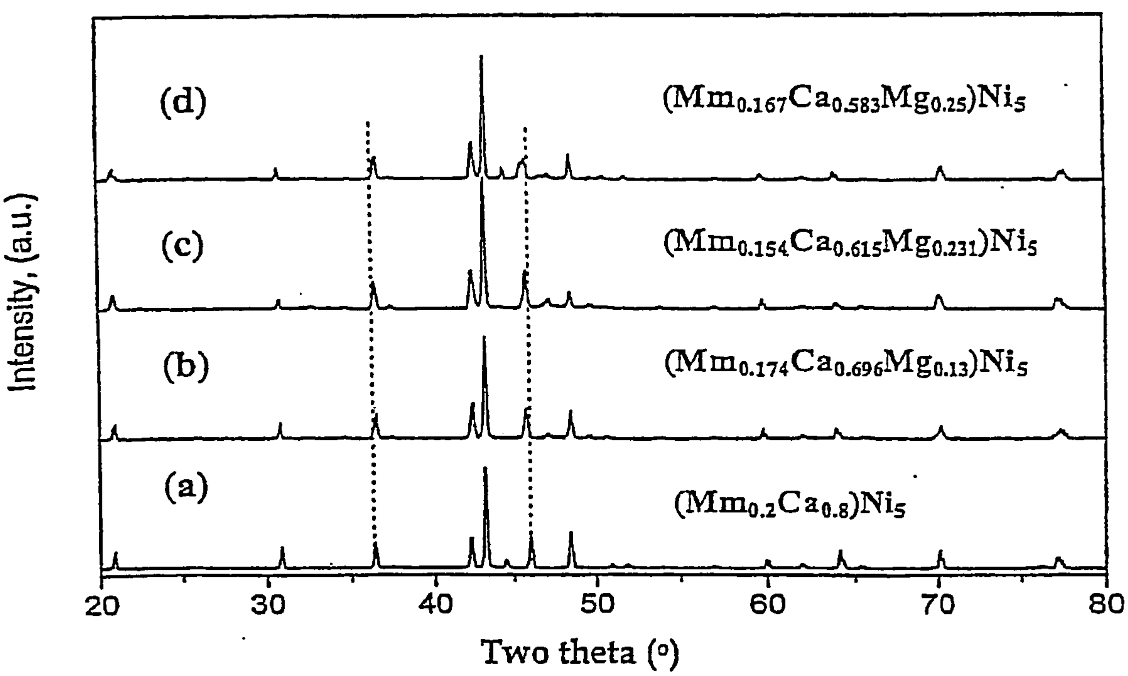
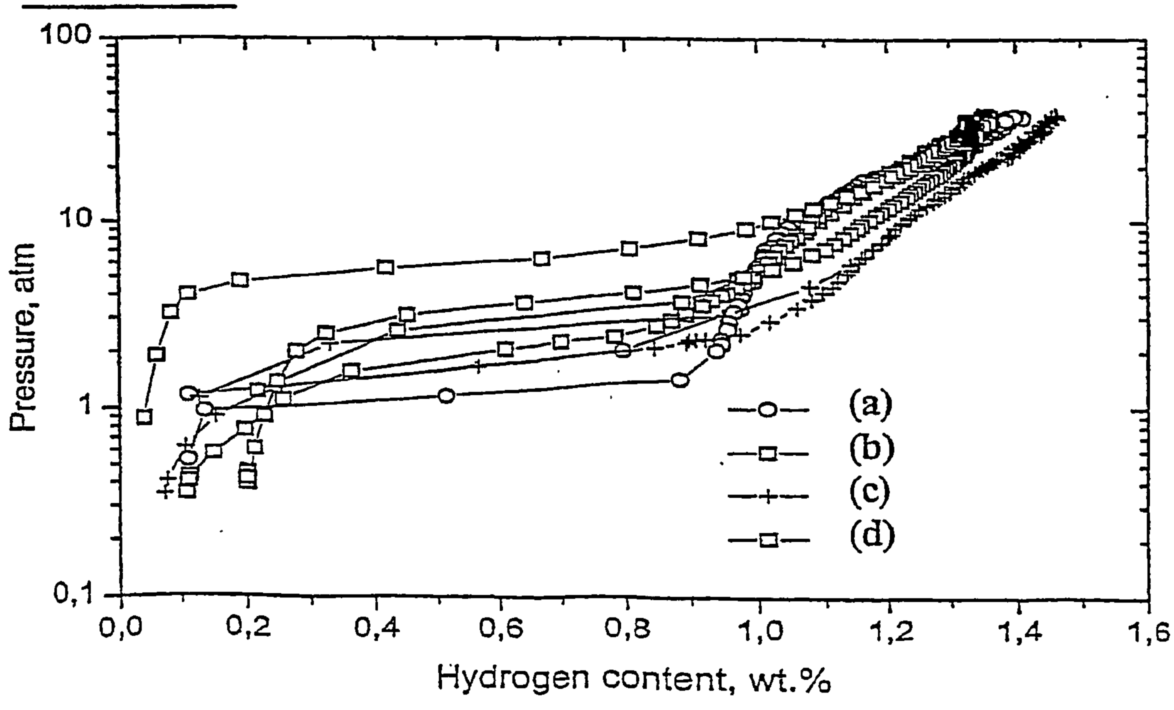
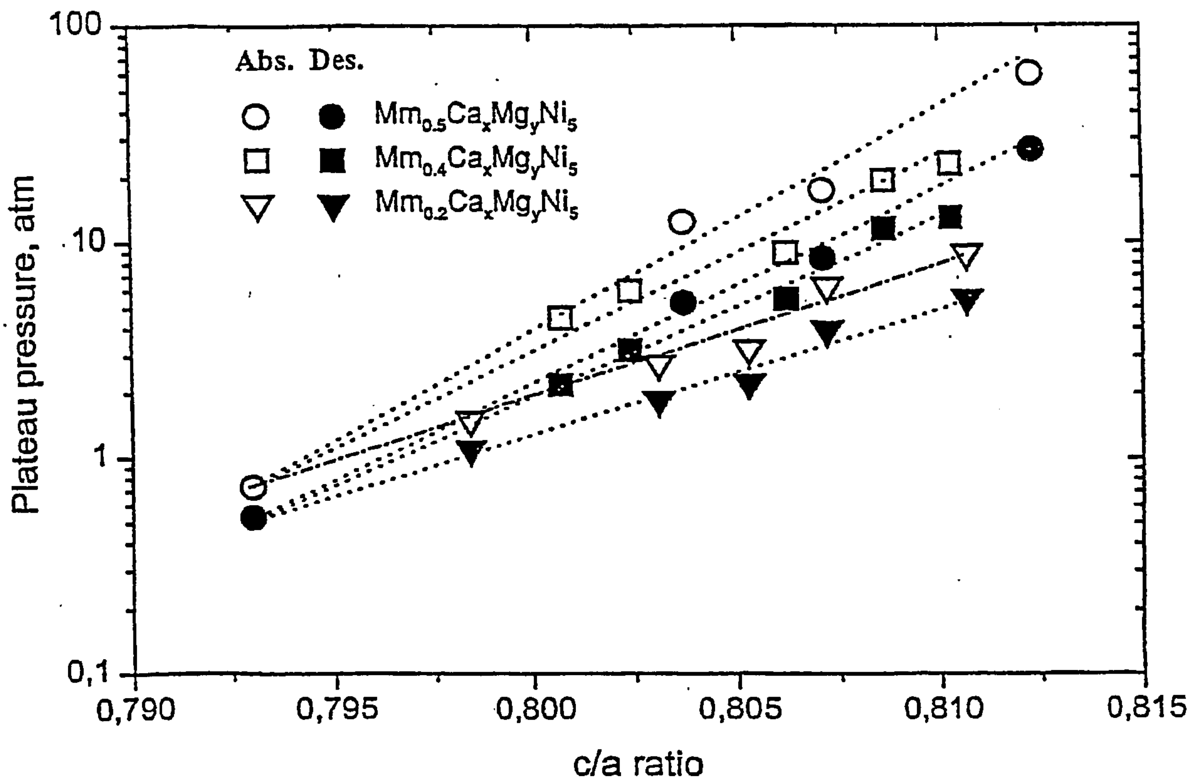


FIG. III-10 b





100
10
1
0,1
Plateau pressure, atm
0,790
0,795
0,800
0,805
0,810
0,815
c/a ratio
Abs. Des.
$Mm_{0.5}Ca_xMg_yNi_5$
$Mm_{0.4}Ca_xMg_yNi_5$
$Mm_{0.2}Ca_xMg_yNi_5$

FIG. III-11

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 03/00058

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22C19/03 C01B6/00 H01M4/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22C C01B H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 892 451 A (TOKYO SHIBAURA ELECTRIC CO) 20 January 1999 (1999-01-20) cited in the application	1,2, 10-13
A	page 3, line 25 - line 28 page 4, line 23 - line 29 page 11, line 23 - line 28 page 26, line 3 - line 7 page 65, line 36 - line 45 example 146; table 18	3
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 06, 22 September 2000 (2000-09-22) -& JP 2000 080429 A (TOSHIBA CORP), 21 March 2000 (2000-03-21) abstract example 11; table 1 example 21; table 3	1-3, 10-13

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
4 July 2003	25.07.03

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Gavriliu, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CA 03/00058

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 08, 5 August 2002 (2002-08-05) -& JP 2002 097535 A (SUMITOMO METAL IND LTD;JAPAN METALS & CHEM CO LTD), 2 April 2002 (2002-04-02) abstract examples 2-10,13,16,17; table 1	1-3, 10-13
A	US 6 268 084 B1 (INADA SHUSUKE ET AL) 31 July 2001 (2001-07-31) column 3, line 31 - line 35 example 100; table 20 examples 113,115,118; table 23 example 131; table 25 example 153; table 28 example 165; table 29	1-3, 10-13
X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 02, 2 April 2002 (2002-04-02) -& JP 2001 303160 A (SUMITOMO METAL IND LTD), 31 October 2001 (2001-10-31)	1,4,6,7
A	abstract examples 1-9,12; table 1	5
A	PATENT ABSTRACTS OF JAPAN vol. 1999, no. 14, 22 December 1999 (1999-12-22) -& JP 11 264041 A (TOSHIBA CORP), 28 September 1999 (1999-09-28) abstract example 18; table 2	1,4-7
A	PATENT ABSTRACTS OF JAPAN vol. 003, no. 037 (C-041), 29 March 1979 (1979-03-29) -& JP 54 011095 A (MATSUSHITA ELECTRIC IND CO LTD), 26 January 1979 (1979-01-26) abstract table	1,4-7
A	US 5 962 165 A (KANDA MOTOYA ET AL) 5 October 1999 (1999-10-05) column 33; examples 10,14; table 4 column 38; examples 24,25; table 7 column 43; example 72; table 12	1,4-7

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/CA 03/00058

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
EP 0892451	A	20-01-1999	CN	1207590	A	10-02-1999
			EP	0892451	A2	20-01-1999
			JP	11323469	A	26-11-1999
			KR	276016	B1	15-12-2000
			US	6130006	A	10-10-2000
JP 2000080429	A	21-03-2000	NONE			
JP 2002097535	A	02-04-2002	NONE			
US 6268084	B1	31-07-2001	JP	11162459	A	18-06-1999
			JP	11162503	A	18-06-1999
			JP	11162460	A	18-06-1999
			US	2001041292	A1	15-11-2001
			KR	276018	B1	15-12-2000
			US	6248475	B1	19-06-2001
JP 2001303160	A	31-10-2001	NONE			
JP 11264041 0	A		NONE			
JP 54011095 0	A		NONE			
US 5962165	A	05-10-1999	JP	9199121	A	31-07-1997
			JP	9199122	A	31-07-1997
			US	2002037454	A1	28-03-2002
			CN	1323071	A	21-11-2001
			CN	1123474	A	29-05-1996
			JP	8311596	A	26-11-1996
			KR	241813	B1	01-02-2000

International application No.
PCT/CA 03/00058

INTERNATIONAL SEARCH REPORT

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.: 1(part), 8,9
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [X] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

1-7, 10-13

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[X] No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1(part), 8,9

The AB2 alloy in claim 1 relates to an extremely large number of possible alloys. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the alloys claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the AB2 type hydrogen storage alloys according to the examples in the description (and figures).

This is also the case for the A2B5 alloy in claim 1.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1,2,3,10-13

   The first alternative of claim 1 relates to an alloy of the general formula: $(Ca_c Mg_d M_e)_b (Ni_{1-z} T_z)_a$ where:

   M is at least one metal selected from the group consisting of Y, Ce, La, Pr, Nd, Th, Nd, Ti, V, Zr, Ta, Hf, Sr, Ba and Misch metals;

   T is at least one element selected from the group consisting of Al, Zn, Cu, Fe, Co, Mn, Cr, Mo, W, Si, Ga, Ge, In, Sn, Ag, C and B;

   a is an integer number equal to 2;
   z is a number ranging from 0 to 0.5, and
   b,c,d,e are numbers selected so that:

   $0.9 \le b \le 1.1$
   $c = 0.4 - x$
   $d = 0.6 - y$
   $e = x + y$
   $-0.5 \le x < 0.4$
   $-0.4 < y \le 0.5$
   and $x+y > 0$

2. Claims: 1, 4-7

   The second alternative of claim 1 relates to an alloy of the general formula: $(Ca_c Mg_d M_e)_b (Ni_{1-z} T_z)_a$ where:

   M is at least one metal selected from the group consisting of Y, Ce, La, Pr, Nd, Th, Nd, Ti, V, Zr, Ta, Hf, Sr, Ba and Misch metals;

   T is at least one element selected from the group consisting of Al, Zn, Cu, Fe, Co, Mn, Cr, Mo, W, Si, Ga, Ge, In, Sn, Ag, C and B;

   a is an integer number equal to 5;
   z is a number ranging from 0 to 0.5, and
   b,c,d,e are numbers selected so that:
   $1.75 \le b \le 2.25$
   $c = 0.4 - x$
   $d = 0.6 - y$
   $e = x + y$
   $-0.4 \le x \le 0.2$
   $-0.2 \le y \le 0.4$
   and $x+y \ge 0$

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

3. Claims: 1,8,9

The third alternative of claim 1 relates to an alloy of the general formula: (Ca c Mg d M e)b (Ni 1-z T z) a
where:

M is at least one metal selected from the group consisting of Y, Ce, La, Pr, Nd, Th, Nd, Ti, V, Zr, Ta, Hf, Sr, Ba and Misch metals:

T is at least one element selected from the group consisting of Al, Zn, Cu, Fe, Co, Mn, Cr, Mo, W, Si, Ga, Ge, In, Sn, Ag, C and B;

a is an integer number equal to 5;
z is a number ranging from 0 to 0.5, and
b,c,d,e are numbers selected so that:
0.75 =< b =< 1.31
c = 0.6 - y
d = x + y
e = 0.4 - x

-0.6 < x < 0.4
-0.4 < y < 0.6
and 0 < x+y =< 0.5